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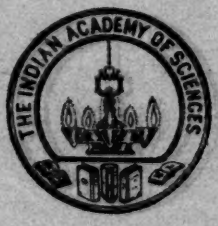

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THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part I. Analysis of the Experimental Data

By Sir C. V. Raman

(*Memoir No. 93 from the Raman Research Institute, Bangalore-6*)

Received December 21, 1956

1. Introduction

It is proposed in this paper to analyze the data for the variation of the specific heat with temperature of some metallic elements. The method of analysis is that already explained and discussed in an earlier paper[1] in these *Proceedings* with reference to the specific heat data for diamond, *viz.*, to determine, with the aid of a table of Einstein's specific heat function, the particular frequency of vibration which if assumed to be common to all the atomic oscillators would give for the specific heat of the substance the actual value observed at any given temperature. The frequency thus calculated is designated as the effective average frequency of the atomic oscillators for that substance at that particular temperature. It is itself a function of the temperature and a graph showing how it varies as we proceed from the highest to the lowest temperatures gives useful indications regarding the distribution of the atomic degrees of freedom of motion over the entire range of frequencies in the vibration spectrum.

The four metallic elements the data for which will be analyzed in this paper are aluminium, copper, silver and lead. They all crystallize in the cubic system in forms based on the so-called face-centred cubic lattice which is really a simple Bravais lattice with only one set of equivalent atoms occupying the corners of a rhombohedral unit cell. We shall make use of the data for the specific heats of these metals determined by Giaque and collaborators.[2] The four metals form a sequence in which the fall of the specific heat at constant volume from the maximum given by the Dulong-Petit formula manifests itself progressively at lower and lower temperatures. There is a special appropriateness in their choice for the present study, since it was the data for these four metals as well as the data for diamond determined by Nernst and Lindmann[3] which were made use of by Debye[4] in a well-known paper as support for his theory of the specific heats of crystals.

2. THE SPECIFIC HEAT DATA

The specific heat data we make use of are plotted as the lower of the two graphs appearing in Figs. 1, 2, 3 and 4 which refer respectively to the four metals aluminium, copper, silver and lead. The absolute temperatures are entered on the scale of abscissæ at the foot of each figure. The scale of ordinates for the specific heats in cal./gm. atom/degree appears on the left-hand side of each figure. The specific heats observed are shown as dotted circles and fall on a smooth curve which touches the axis of abscissæ at the lowest temperatures and tends to approach the maximum limit at higher temperatures. The scale of ordinates used for the specific heats is rather too small for the values at the very lowest to be adequately represented. The slope of the specific heat curve at the upper end of the temperature range is greatest for aluminium, less for copper, still less for silver, while for lead it is almost indistinguishable from a horizontal straight line.

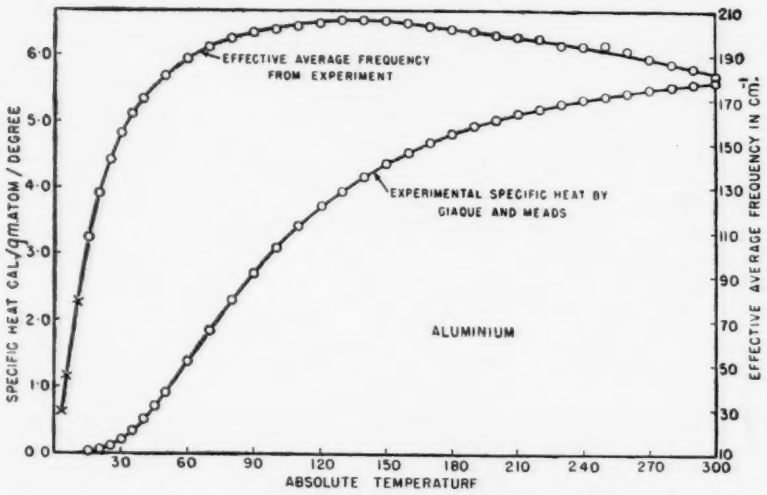

FIG. 1. Analysis of the Specific Heat of Aluminium.

3. THE EFFECTIVE AVERAGE FREQUENCY

The upper of the two graphs in each of the four figures represents the average effective frequency of the atomic oscillators calculated in the manner already explained. The frequencies are shown in the usual spectroscopic nomenclature as wave-numbers and the scale of ordinates for the same appears on the right-hand side of each figure. The calculated values are shown as dotted circles and a smooth curve has been drawn through them. It will

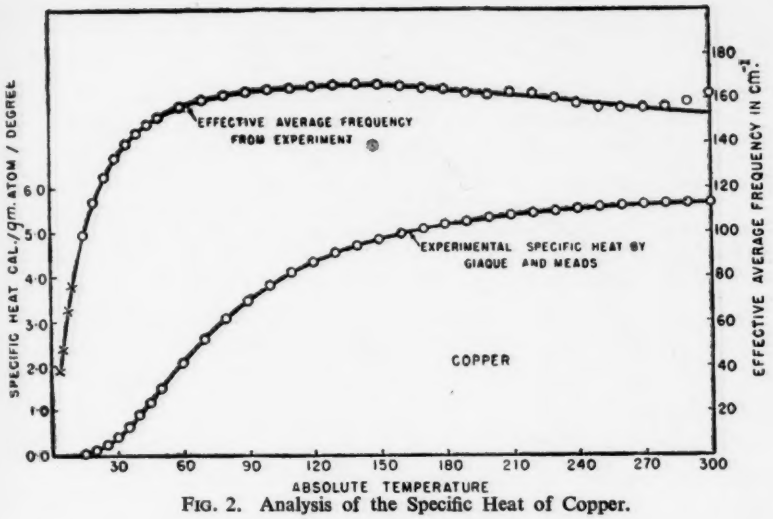

FIG. 2. Analysis of the Specific Heat of Copper.

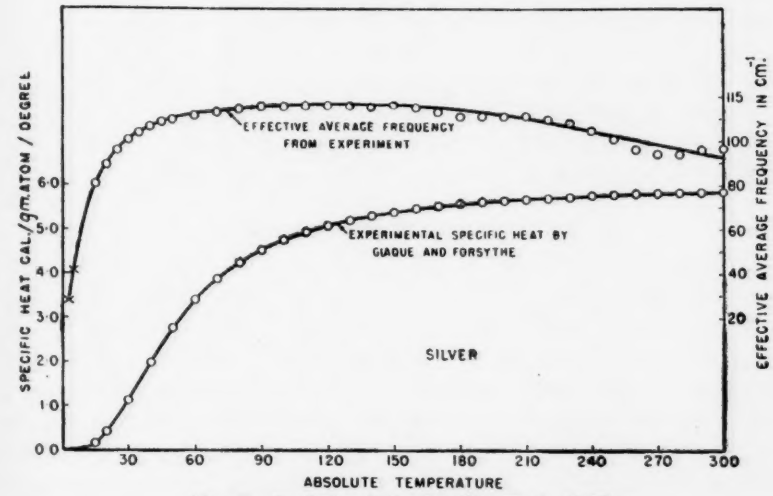

FIG. 3. Analysis of the Specific Heat of Silver.

be seen that they exhibit a certain amount of scatter in the higher parts of the temperature range in each case. This is not surprising, since a very small error in the determination of the specific heat at this part of the range would represent a large error in the calculation of the effective average frequency.

The graphs have been drawn as smooth curves to represent the general trend of the calculated values, ignoring the accidental fluctuations.

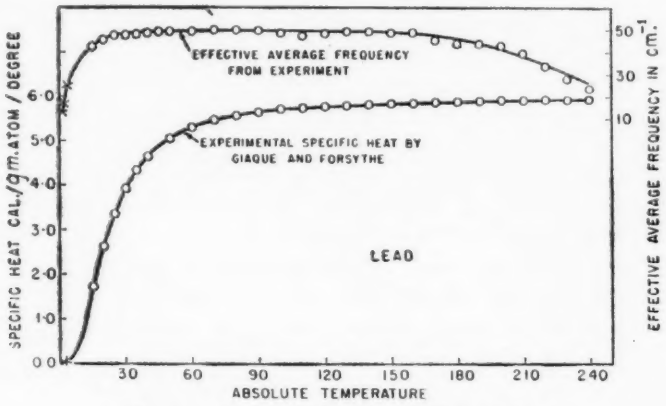

FIG. 4. Analysis of the Specific Heat of Lead.

It appeared important to continue the graphs to still lower temperatures than those covered by determinations by Giaque and collaborators. Accordingly, we have made use of the data obtained by other authors[6–7] for determining the effective average frequency of the atomic oscillators in this lowest part of the temperature range. The computed frequencies are shown as crosses on the extreme left-hand side of the figure in each case and the graphs have been prolonged so as to pass smoothly through those points.

4. THE SIGNIFICANCE OF THE RESULTS

On a comparison of the frequency-temperature graphs for the four metals, it will be seen at once that while there are certain general similarities, there is also a progressive change in form as we go down the series. All the four curves show a maximum in the middle part of the temperature range covered by the data. This maximum can be located pretty definitely at about 135° K. for aluminium. In the case of the other three metals, it becomes progressively more difficult to fix upon a definite temperature as the location of the maximum, the graph being practically a horizontal straight line over an increasingly larger range of temperatures. In other words, the effective average frequency of the oscillators has a practically constant value over a wide range of temperatures. This frequency (in wave-numbers) is 206 for aluminium, 167 for copper, 113 for silver and 50 for lead.

The shape of the graph at low temperatures recalls the course of the graph in the case of diamond already described and discussed in detail in the earlier paper already cited. It is sufficient here to remark that the progressively steeper fall of the graph to low frequencies with the fall of temperature is a consequence of the contribution to the specific heat made by the atomic vibrations of higher frequencies dropping out progressively, until finally at the lowest temperatures we are left only with the contribution made by the vibrations of the very lowest frequencies.

The horizontal stretch of the curves in the middle parts of the temperature range is very clearly analogous to that appearing in the case of diamond throughout the higher parts of the temperature range. Hence, as in the case of diamond, we infer that in this region the effective average frequency of the atomic oscillators is the same or nearly the same as the arithmetical average of the atomic vibration frequencies, the latter term having the same significance as in the discussion of the data for diamond.

5. Frequency Changes at the Higher Temperatures

We turn next to consider the course of the curve in the higher parts of the temperature range. We may reject any interpretation of the features which it exhibits as arising from errors in experimental data. For, the same phenomenon is shown by all the four metals in the same temperature range but to different extents, as is to be expected. Hence, the only possible interpretation of the drop in the effective average frequency at the higher temperatures shown by the graphs is that the atomic vibration frequencies are themselves a function of the temperature and progressively diminish as the temperature rises. It is not possible from the specific heat data to infer what the rate of such diminution is in the lower parts of the temperature range. But we can definitely infer from the form of the curves at the higher temperatures that the fall of the atomic vibration frequencies with rising temperature is at first rather slow, but that it accelerates and finally reaches a fairly steady rate at the higher temperatures.

The detailed discussion of the effects thus brought to light by our present analysis is more appropriately dealt with in Part II of the present paper which concerns itself with the theoretical evaluation of the specific heats of metals as a function of temperature. We may, however, briefly record here some numerical results regarding the rate of fall of the atomic vibration frequencies (expressed as a fraction thereof per degree centigrade) which may be deduced from the slope of the graphs in the case of these four metals. As already remarked, this temperature coefficient is not a constant and we have therefore to consider its value in the vicinity of some temperature at which

the graph has a fairly uniform slope. The values deduced in this way are given below in round figures, and represent the quantity $\frac{1}{\nu}\frac{\Delta\nu}{\Delta T}$, ν being the effective average frequency of the atomic oscillators. The figures for copper, silver and lead indicate a rather steep increase in the temperature coefficients of the atomic vibration frequencies with increasing atomic mass.

Substance	Atomic Weight	Temperature	Temperature Coefficient of Frequency
Aluminium ..	27·0	255° K.	10×10^{-4} per degree
Copper	63·6	250° K.	6×10^{-4} ,, ,,
Silver	107·9	270° K.	21×10^{-4} ,, ,,
Lead	207·2	215° K.	99×10^{-4} ,, ,,

6. SUMMARY

The specific heat data in the temperature range from 15° to 300° reported by Giaque and collaborators for the four metals aluminium, copper, silver and lead are analysed and the effective average frequency of the atomic oscillators deduced therefrom is plotted as a function of the temperature. The graphs exhibit a steep fall of the effective frequency at very low temperatures as is to be expected. In the middle part of the temperature range, the frequency exhibits a broad maximum which in spectral wave-numbers is respectively 206, 167, 113 and 50 for the four metals. At higher temperatures the graph exhibits a second fall which indicates that there is a real and progressive diminution of the actual vibration frequencies of the atoms in the crystal with rising temperature in this range. The effect becomes increasingly more pronounced with increasing atomic mass.

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THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part II. Approximate Theoretical Evaluation

By Sir C. V. Raman

(*Memoir No. 93 from the Raman Research Institute, Bangalore-6*)

Received January 3, 1957

1. Introduction

In this second paper of the series, we consider the problem of evaluating the specific heats of the four metals aluminium, copper, silver and lead, making use of the theroretical ideas set forth in an earlier paper in these *Proceedings*.[1] The metallic atoms in all these four cases are located at the equivalent points of a simple Bravais lattice of which the unit cell is a rhombohedron. Accordingly, all the normal modes of vibration are of the second kind, namely, those in which the successive atoms along one, two or all the three axes of the lattice oscillate with equal amplitudes but with opposite phases. By simple inspection of a model of the structure, it can be seen that the twenty-one possible normal modes of this kind group themselves into only four distinct modes with 3, 6, 4 and 8 as their respective degeneracies. These may be described in simple geometric terms: oscillations of the atoms in the cubic planes along the normals to those planes (degeneracy 3); oscillations of the atoms in the cubic planes tangential to those planes (degeneracy 6); oscillations of the atoms in the octahedral planes normal to those planes (degeneracy 4); oscillations of the atoms in the octahedral planes tangential to those planes (degeneracy 8). Accordingly, the specific heat of these metals is obtained by a summation of the Einstein functions for the frequencies of these four modes multiplied by their respective degeneracies. To this must be added the contribution arising from the spectrum of vibrational frequencies with a statistical weight of three arising from the three translations of the unit cell with the 8 atoms at its corners. This contribution appears as an integration of Einstein functions taken over a continuous spectrum of frequencies, the upper limit of frequency in the integration being the lowest of the four characteristic frequencies.

2. Evaluation of the Characteristic Frequencies

Each of the atoms in a face-centred cubic lattice has twelve nearest neighbours, six second neighbours, twenty-four third neighbours and twelve

fourth neighbours. The six constants needed to determine the force on any one atom resulting from the displacement of another atom reduce, by virtue of the symmetry of the structure, to *three* constants in the case of the nearest neighbours, *two* constants for the second neighbours, *four* constants for the third neighbours and so on. Thus, even if only the first three sets of neighbours are considered, the equations of motion of an atom would involve nine force-constants arising from the displacements of the surrounding atoms. In the absence of any knowledge regarding the magnitudes of these nine constants, it is not possible to evaluate the four frequencies which we need to know. In the case of diamond dealt with in an earlier paper in the *Proceedings*, it was possible to proceed on the basis of its known spectroscopic behaviour and to make an independent evaluation of the eight characteristic frequencies of vibration of its structure. It is obvious that a different procedure has to be adopted in the case of the metallic elements.

What we have to ascertain are the frequencies of vibration of the atomic *layers* lying respectively in the cubic and octahedral planes normally or tangentially to themselves. It is evident that the frequencies of such vibration would depend on the integrated effect on any one *layer* of the movements of the neighbouring layers. Various considerations indicate that the force acting on any layer would be determined *principally by the displacements relatively to that layer of the two neighbouring layers lying one on either side of it*. By way of justifying this statement, we remark that the first, second and third neighbours of any one atom are mostly to be found either in the same layer or in the two adjacent layers. For instance, in the cubic layers all the twelve near neighbours, four out of the six second neighbours and sixteen out of the twenty-four third neighbours are to be found thus located. Likewise, in the octahedral layers all the twelve near neighbours, all the six second nearest neighbours and eighteen out of the twenty-four third neighbours are to be found thus located. Hence, the frequencies of oscillation with which we are concerned may *as a first approximation* be evaluated on the basis that the forces on any one layer arise only from the displacements relative to it of the two neighbouring layers, one on either side of it.

For the same reasons as those explained above, the forces which determine the velocities of elastic wave propagation in the cubic and octahedral directions would likewise be determined *as a first approximation* by the displacements relative to any layer of the two neighbouring layers one on either side. Hence, we are in a position to establish simple but approximate relationships between the characteristic frequencies of vibration of the

lattice and the velocities of propagation of elastic waves (longitudinal or transverse as the case may be) in the directions normal to the cubic and octahedral planes respectively. This relation may be written as below:

$$\text{Characteristic frequency} = \frac{2}{\pi} \cdot \frac{\text{Velocity of long elastic waves}}{\text{Twice the distance between adjacent layers}}.$$

The correctness of the formula is easily verified by comparison with the case of a simple linear lattice, *viz.*, a string under tension loaded with identical mass-particles at equidistant intervals.

3. Numerical Results

The foregoing approximate relationships between the velocity of propagation of elastic waves along the octahedral and cubic axes and the characteristic frequencies of a face-centred cubic lattice enable us to evaluate the latter for those crystals for which the elastic constants have been determined with precision. The published determinations make use of the three constants C_{11}, C_{12} and C_{44} contemplated in Voigt's theory. The four velocities we are concerned with are the square roots of C_{11}/ρ, C_{44}/ρ

$$(C_{11} + 2\,C_{12} + 4\,C_{44})/3\rho \text{ and } (C_{11} - C_{12} + C_{44})/3\rho.$$

In the cases of aluminium[2] and copper,[3] the values of C_{11}, C_{12} and C_{44} are available over a wide range of temperatures from the very lowest upwards. They exhibit a progressive diminution with temperature, which at first is slow but accelerates at high temperatures. In the cases of silver[4] and lead,[5] however, determinations of the elastic constants only at room temperatures are available and we shall make use of them.

Table I

Characteristic frequencies in wave-numbers

Mode	Degeneracy	Aluminium		Copper		Silver	Lead
I	3	353	340	260	255	179	88
II	6	177	169	177	171	109	48
III	4	287	302	269	263	179	87
IV	8	145	138	113	109	70	30
Average	..	211	207	182	177	117	54

Table I shows the four characteristic frequencies calculated in the manner explained above. In the cases of aluminium and copper, the values are given at absolute zero as also at room temperature, while in the case of silver and lead, only room temperature values are given. Multiplying the frequencies by the degeneracies of the respective modes, then adding up and dividing by 21, we get the arithmetical average of the four frequencies. This is shown at the foot of the table in each case.

As the elastic constants diminish with increasing temperature but not all in the same manner, it is not altogether surprising to find that one of the calculated frequencies for aluminium actually increases instead of diminishing with rise of temperature. However, both for aluminium and for copper the arithmetical average shows a noticeable fall at room temperature as compared with the value at the absolute zero.

4. CALCULATION OF THE SPECIFIC HEATS

The expression for the thermal energy of the crystal is given by the formula

$$\frac{N}{8}\left\{\sum_{i=1}^{i=4}\frac{h\nu_i}{e^{h\nu_i/kT}-1}+\frac{3}{\nu_4{}^3}\int_0^{\nu_4}\frac{h\nu}{e^{h\nu/kT}-1}\,3\nu^2\,d\nu\right\}$$

where N is the number of lattice cells contained in the volume of the crystal under consideration. Differentiating this with respect to T, we obtain the specific heat of the crystal at any given temperature. In evaluating the same, we make use of the tabulated values of the well-known functions appearing in the expressions.

The values of the specific heat have been plotted as functions of the absolute temperature in the lower of the two graphs in Figs. 1, 2, 3 and 4 which refer respectively to the four metals. As usual, the abscissæ are the absolute temperatures, and the scale of ordinates for the specific heat appears on the left-hand side of the figure in each case. The upper graph in each figure is the effective average frequency determined from the calculated specific heat in the manner already explained in the previous papers. The scale of ordinates for this frequency appears on the right-hand side of the figure in each case and is expressed in wave-numbers.

It will be noticed that at the upper end of the temperature range in each of the four cases, the effective average frequency of the atomic oscillators deduced from the calculated specific heats is respectively 210, 182, 117 and 55 cm.$^{-1}$ It will also be noticed that these are equal respectively to the

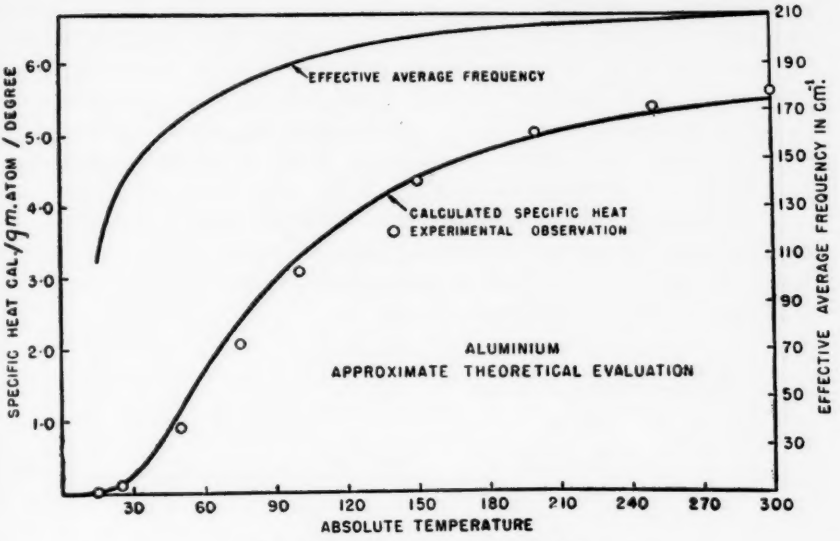

FIG. 1. Specific Heats of Aluminium.

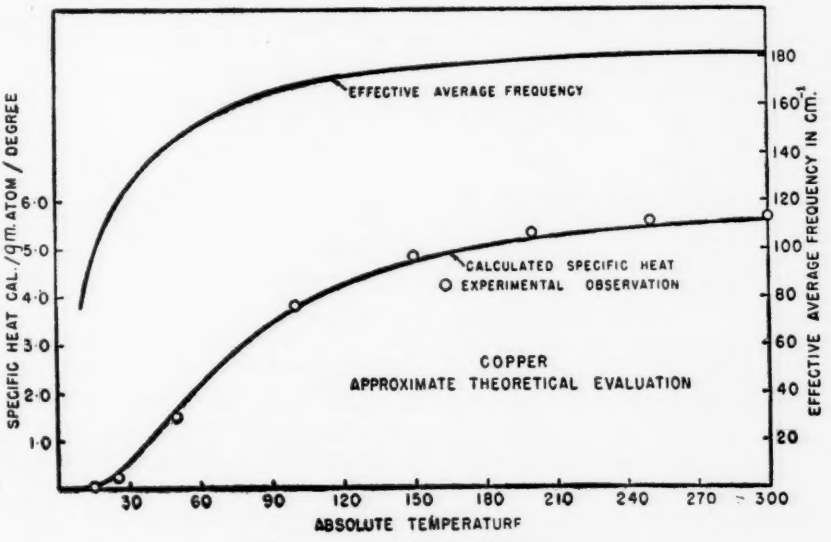

FIG. 2. Specific Heats of Copper.

arithmetical average of the four characteristic frequencies of each metal shown at the foot of Table I. The effective average frequency falls off quite slowly as the temperature goes down and hence in the upper part of the temperature range, the arithmetical average frequency determines the course of the specific heat curve. Hence any assumption, however arbitrary, regarding the nature of the atomic vibration spectrum would give the specific heat correctly in this part of the range, provided it gives the same arithmetical average for the atomic vibration frequencies. It is only the steeply falling part of the specific heat curve that is sensitive to the precise nature of the assumed vibration spectrum and can furnish reliable information regarding its true complexion.

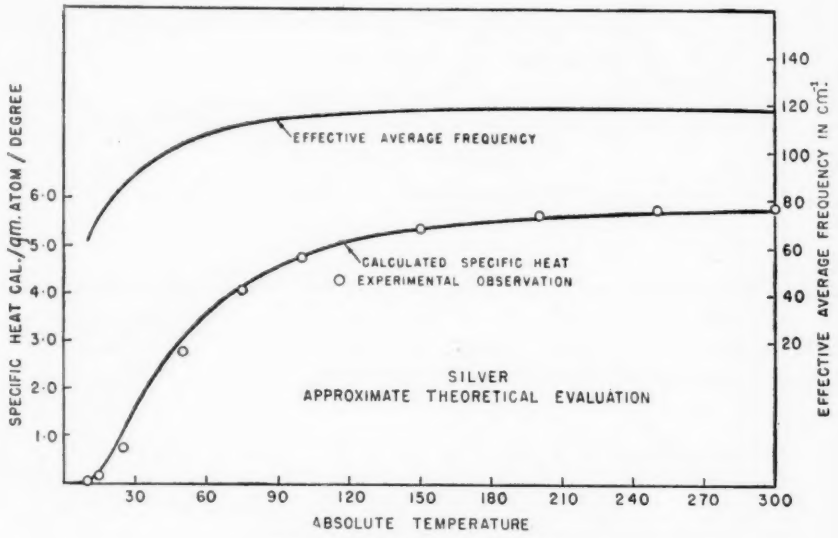

FIG. 3. Specific Heats of Silver.

5. DISCUSSION OF THE RESULTS

In Part I of the present series of papers,[6] an analysis of the results of the specific heat determinations by Giaque and his collaborators for these four metals was presented and graphs were reproduced showing the effective average frequency as a function of the temperature. These graphs, unlike those appearing in the present paper, do *not* appear as nearly horizontal lines in the upper part of the temperature range in each case, but exhibit a

plateau* in the middle part of the range and then slope down to lower values at the upper limit of the range. It is to be inferred from these consequences deduced from the actual specific heat determinations that the atomic vibration frequencies are themselves not independent of the temperature, and that they (or at least their arithmetical averages) diminish progressively as the temperature rises.

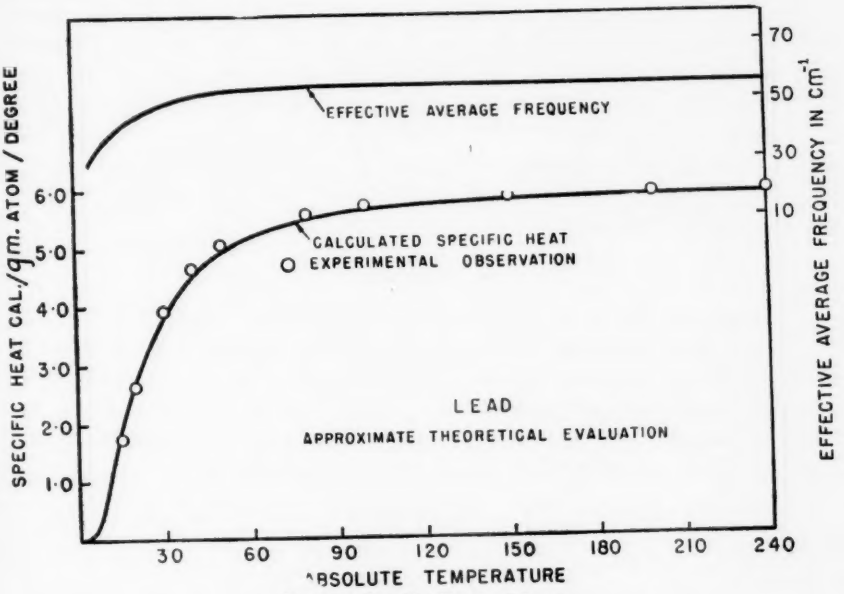

FIG. 4. Specific Heats of Lead.

The experimentally determined specific heats[7,8] have been plotted alongside of the graphs of the calculated specific heats in Figs. 1, 2, 3 and 4 of the present paper. In view of the remarks made above, it is to be expected that the observed specific heats would lie above the calculated ones in the upper part of the temperature range. It will be noticed from the figures that this is actually the case. The deviations are fairly conspicuous in the case of aluminium and copper, but are less conspicuous in the cases of silver and lead. The characteristic frequencies for aluminium and copper were calculated from the low-temperature elastic constants, while for silver and lead the frequencies were calculated from the elastic constants at room

* The plateau frequencies are 206, 167, 113 and 50 cm.$^{-1}$ respectively for aluminium, copper, silver and lead. These are somewhat smaller than the arithmetical average frequencies, as is to be expected.

temperature. The closer approximation actually found between the observed and the calculated specific heats for silver and lead at the higher temperatures is therefore to be expected.

Having regard to the method used for evaluating the four characteristic frequencies, and remembering also that in the present theory we have totally disregarded the anharmonicity of the atomic oscillators, the general agreement between theory and observation over the entire range of temperatures exhibited by Figs. 1 to 4 may be considered satisfactory. However, it is to be remarked that the observed specific heats are sensibly lower than the calculated ones in the range of temperatures where the specific heat curve slopes steeply down. This is noticeable in the cases of all the four metals and indicates that the characteristic frequencies as determined by the present approximate method need revision. We shall return to this in the third paper of the series.

6. SUMMARY

The specific heats of the four metals aluminium, copper, silver and lead which crystallise as face-centred cubic lattices are evaluated in terms of the four characteristic frequencies of vibration of such a lattice, these latter being determined by an approximate method which relates them to the elastic constants of the crystal. The results thus derived are discussed and compared with the experimentally determined specific heats.

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CONSTITUTION OF DALBERGIN

Part III. Synthesis of Dalbergin, Iso-Dalbergin and Their Ethers

By V. K. Ahluwalia, A. C. Mehta and T. R. Seshadri, F.A.Sc.

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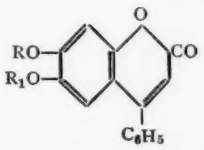
Received November 15, 1956

In Part II[1] it was shown that dalbergin is a monomethyl ether of 4-phenyl aesculetin. The position of the methoxy group has now been established by the synthesis of 7-methoxy-6-ethoxy-4-phenyl coumarin (I) and 7-ethoxy-6-methoxy-4-phenyl coumarin (II); the former agreed in every respect with 0-ethyl dalbergin and hence the constitution of dalbergin should be that of 4-phenyl aesculetin-7-methyl ether (III).



I, $R=CH_3$, $R_1=C_2H_5$
II, $R=C_2H_5$, $R_1=CH_3$
III, $R=CH_3$, $R_1=H$
IV, $R=R_1=H$
V, $R=H$, $R_1=CH_3$

For the preparation of the above-mentioned mixed ethers nuclear oxidation with alkaline persulphate has been employed. 4-Phenyl-7-methoxy coumarin yields the 6-hydroxy compound (III) which is ethylated to form the 6-ethoxy compound (I). Using 7-ethoxy-4-phenyl coumarin instead and finally methylating the nuclear oxidation product, the isomeric-7-ethoxy-6-methoxy-4-phenyl coumarin (II) has been prepared. In the course of these preparations, the intermediate 7-methoxy-6-hydroxy-4-phenyl coumarin (III) has been found to be identical with dalbergin. Another method of synthesis involves partial methylation of 4-phenyl aesculetin (IV) using dimethyl sulphate and sodium bicarbonate. That such partial methylation is possible in the 7-position has already been shown in connection with 4-methyl aesculetin[2] and 4-methyl-5:7-dihydroxy coumarin.[3] Partial ethylation is also successful and provides an alternative method for the preparation of 7-0-ethyl-4-phenyl aesculetin and the mixed ether (II).

6-Methoxy-7-hydroxy-4-phenyl coumarin (iso-dalbergin) (V) would be analogous to scopoletin and may be expected to occur in nature. Its synthesis has been carried out through the intermediate 6-hydroxy-7-benzyloxy compound, which has been prepared by two methods: (1) nuclear oxidation of 7-benzyloxy-4-phenyl coumarin, and (2) partial benzylation of

4-phenyl aesculetin (IV). Further stages involve methylation of 7-benzyloxy-6-hydroxy-4-phenyl coumarin and subsequent debenzylation. The identity of iso-dalbergin has been confirmed by its ethylation to yield the mixed ether (II).

The earlier method for the preparation of 4-phenyl aesculetin[1] (IV) employed hydroxy quinol acetate and the Pechmann condensation with benzoyl acetic ester. As an alternative method the nuclear oxidation of 4-phenyl umbelliferone has been explored. The method is successful though the yield is not good.

EXPERIMENTAL

0-*Ethyl dalbergin* was prepared by ethylation of dalbergin[1] with diethyl sulphate and potassium carbonate in acetone solution. It crystallised from methyl alcohol as colourless long rhombohedral plates, m.p. 163–64° (Found: C, 72·8; H, 5·4; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%.)

4-*Phenyl*-6-*hydroxy*-7-*methoxy coumarin* (*Dalbergin*) (*III*)

(*a*) *Partial methylation of* 4-*phenyl aesculetin* (*IV*).—4-Phenyl aesculetin[1] (2 g.) was refluxed in dry acetone (300 c.c.) with dimethyl sulphate (0·75 c.c.) and sodium hydrogen carbonate (4 g.) for 24 hours, the acetone solution filtered, and the inorganic salts washed with hot acetone (50 c.c.). The solvent was distilled off and the residue treated with water. The solid crystallised first from methanol and finally from ethyl acetate as colourless rhombohedral prisms (1·5 g.), m.p. 210–11°, undepressed by an authentic sample of dalbergin.[4] Its colour reactions were the same as those of natural dalbergin. The acetate, methyl ether and ethyl ether of the above 4-phenyl-6-hydroxy-7-methoxy coumarin melted at 158-59°, 144–45° and 163–64° respectively and agreed in all respects with acetyl dalbergin,[4] 0-methyl dalbergin[1, 4] and 0-ethyl dalbergin respectively.

(*b*) *Nuclear oxidation of* 4-*phenyl*-7-*methoxy coumarin*.—4-Phenyl-7-methoxy coumarin is conveniently prepared by the methylation of 4-phenyl umbelliferone[5] using the dimethyl sulphate-potassium carbonate-acetone method, m.p. 116–18°. It (5 g.) was refluxed with aqueous sodium hydroxide (5 g. in 100 c.c. water) for two hours. The solution was cooled (15–20°), stirred and treated dropwise with potassium persulphate (9 g. in 200 c.c. water) during two hours. After twenty-four hours at room temperature the deep brown solution was acidified to congo-red and the unchanged product filtered off, ether extration removing the last traces of it. The clear brown solution was heated in a boiling water-bath with sodium sulphite (5 g.) and concentrated hydrochloric acid (100 c.c.) for half an hour. After

cooling the solid product was filtered and crystallised from methyl alcohol (2·7 g.); m.p. 210–11°, undepressed by an authentic sample of dalbergin.[4]

4-*Phenyl-7-ethoxy coumarin.*—4-Phenyl-7-hydroxy coumarin[5] (10 g.) was refluxed with diethyl sulphte (9 c.c., excess), potassium carbonate (20 g.) and acetone (150 c.c.) for six hours. The product crystallised from methyl alcohol yielding colourless rectangular plates (9·0 g.), m.p. 104–05° (Found: C, 76·1; H, 5·3; $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

4-*Phenyl-6-hydroxy-7-ethoxy coumarin.*—It was prepared by the nuclear oxidation of the above 4-phenyl-7-ethoxy coumarin (5 g.) in aqueous sodium hydroxide (5 g. in 100 c.c. water) with potassium persulphate (9 g.) as in the earlier case. It crystallised from ethyl acetate-petroleum ether mixture as pale yellow rectangular tablets (1·2 g.), m.p. 156–57.° (Found: C, 71·6; H, 5·1; $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%.) The acetate prepared with acetic anhydride and pyridine crystallised from benzene petroleum ether mixture as colourless lance-shaped crystals, m.p. 108–09°.

4-*Phenyl-6-methoxy-7-ethoxy coumarin* (II).—The above 6-hydroxy compound (0·5 g.) was refluxed in dry acetone (75 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (2 g.) for six hours. The product crystallised from methyl alcohol as colourless prismatic needles (0·4 g.), m.p. 106–08°. (Found: C, 72·7; H, 5·7; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%.)

4-*Phenyl-7-benzyloxy coumarin.*—4-Phenyl-7-hydroxy coumarin[5] (12 g.) in acetone (200 c.c.) was refluxed with anhydrous sodium iodide (10 g.), benzyl chloride (7 c.c.) and potassium carbonate (15 g.) for eight hours, the acetone solution filtered and the inorganic salts washed with more of hot acetone. The solvent was distilled off and the excess of benzyl chloride removed by steam distillation. The benzyl ether crystallised from ethyl acetate and light petroleum mixture as colourless needles and narrow rectangular plates (8 g.), m.p. 91–92°. (Found: C, 80·6; H, 5·2; $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%.)

4-*Phenyl-6-hydroxy-7-benzyloxy coumarin*

(*a*) *Nuclear oxidation of* 4-*phenyl-7-benzyloxy coumarin.*—4-Phenyl-7-benzyloxy coumarin (5 g.) was oxidised with potassium persulphate (9 g.) in sodium hydroxide solution (100 c.c., 5%) as in the earlier cases. The product crystallised from benzene yielding colourless prismatic needles (0·7 g.), m.p. 213–14°. (Found: C, 76·2; H, 4·8; $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%.) The acetate prepared with acetic anhydride and pyridine

crystallised from methyl alcohol as colourless thick rectangular, plates m.p. 159–60°.

(*b*) *Partial benzylation of* 4-*phenyl aesculetin.*—4-Phenyl aesculetin[1] (3 g.) in acetone (150 c.c.) was refluxed with sodium iodide (4 g.), benzyl chloride (0·9 c.c.) and sodium bicarbonate (4 g.), for twenty-four hours. Acetone was distilled off and the residue treated with water; the solid product crystallised first from ethyl alcohol and finally from ethyl acetate (1·5 g.); m.p. 213–14°. Mixed m.p. with the product obtained in (*a*) was undepressed.

4-*Phenyl*-6-*methoxy*-7-*benzyloxy coumarin* was prepared by refluxing the above 6-hydroxy-coumarin (1 g.) in acetone (150 c.c.) with dimethyl sulphate (0·4 c.c.) and potassium carbonate (1 g.). The product crystallised from ethyl alcohol as colourless long prisms (1 g.), m.p. 196–98°. (Found: C, 76·9; H, 5·6; $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·1%.)

4-*Phenyl*-6-*methoxy*-7-*hydroxy coumarin* (*Iso-dalbergin*).—The foregoing compound (0·5 g.) was dissolved in glacial acetic acid (15 c.c.), concentrated hydrochloric acid (15 c.c.) added, and the solution heated on a steam-bath for one hour. Acetic acid, benzyl chloride and hydrochloric acid were completely distilled off under reduced pressure and the residue washed with a small amount of petroleum ether to remove the last traces of benzyl chloride. Crystallisation from ethyl acetate-petroleum ether mixture yielded colourless shining very thin rectangualr plates (0·25 g.), m.p. 195–96°. (Found: C, 72·0; H, 4·8; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%.) The acetate prepared with acetic anhydride and pyridine crystallised from ethyl alcohol yielding colourless short prismatic meedles, m.p. 171–72°. The ethyl ether prepared by ethylation of the above coumarin with ethyl sulphate and potassium carbonate in acetone medium crystallised from methyl alcohol, m.p. 106–08° undepressed by the sample of 4-phenyl-6-methoxy-7-ethoxy coumarin reported earlier.

4-*Phenyl*-6: 7-*dihydroxy coumarin* (*Nor-dalbergin*) (*IV*).—4-Phenyl-7-hydroxy coumarin[5] (5 g.) was dissolved in aqueous sodium hydroxide (5 g. in 100 c.c. water) and oxidised with potassium persulphate (9 g. in 200 c.c. water). The product crystallised from methyl alcohol as colourless small rectangular tablets and tiny prisms (0·8 g.), m.p. 268–69°, undepressed by an authentic sample of nor-dalbergin.[1, 4] The acetate and the methyl ether melted at 157–58° and 144–45° respectively and agreed in all respects with acetyl nor-dalbergin[1, 4] and methyl dalbergin[1, 4] respectively.

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Summary

The position of the methoxyl group in dalbergin has been established by synthesis using two methods: (1) partial methylation of 4-phenyl-aesculetin and (2) nuclear oxidation of 4-phenyl umbelliferone methyl ether. By similar methods the 7-benzyl ether of 4-phenyl aesculetin and from it by methylation and debenzylation iso-dalbergin has been prepared. The ethyl ethers of dalbergin and iso-dalbergin have also been obtained.

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PREPARATION OF PURE U_3O_8 FROM CRUDE SODIUM DIURANATE BY INTERMEDIATE COMPLEX FORMATION

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Separation of uranium from various undesirable elements is usually done by solvent extraction[1,2] and several other complexing procedures.[3,4] Bolton[5] and Baker[6] have reported the formation of soluble complexes of the type $M_3UO_2F_5$ ($M = K$, NH_4, $\frac{1}{2}Ba$) which are oxidized by hydrogen peroxide in aqueous solutions to insoluble per-compounds[7] of the type $M_4U_4O_{15}F_6.xH_2O$. Preliminary studies have been made for the separation of uranium from thorium, rare earths and iron, making use of the above complexes, and the results are given below.

Nitrate solutions of uranium, thorium, rare earths and iron were mixed together and potassium fluoride (or ammonium fluoride) was added slightly in excess of that required for complexing the above elements. Fluorides of thorium and rare earths got precipitated while those of uranium and iron remained in solution in the form of soluble complexes. The precipitate was washed with water to recover all uranium. Conditions of pH required to prevent precipitation of uranium together with thorium and rare earths fluorides were studied and the results are given in Table I.

The solution after the removal of thorium and rare earths was treated with enough hyrogen peroxide to precipitate the per salt (the composition of which is to be established) of the uranium complex $M_3UO_2F_5$. The influence of pH on the complete precipitation of uranium free from iron was investigated and the results are given in Table II.

The effect of change in concentrations of thorium, rare earths and iron on the separation of uranium was also studied and the results are given in Table III.

Employing the above procedure, crude sodium diuranate (50 g.) containing ThO_2 0·4%; Rare earth oxides 1·7%; Fe_2O_3 0·6%; SiO_2 0·62%; and U_3O_8 78·2% was converted to uranium oxide which on analysis gave the

TABLE I

Effect of pH on the separation of uranium from thorium and rare earths

U_3O_8 mg.	ThO_2 mg.	Oxides of rare earths mg.	pH initial	pH adjusted before KF addition	pH of filtrate after removal of insoluble fluorides	U_3O_8 in the filtrate mg.	Oxides of thorium and rare earths in the ppt. of fluorides mg.
392·3	5·98	4·0	2·64	2·1	4·74	391·0	10·0
392·3	5·98	4·0	2·64	2·64	4·86	391·4	9·95
392·3	5·98	4·0	2·64	3·0	5·57	390·5	10·02
392·3	5·98	4·0	2·64	4·04	6·68	..	..*
392·3	5·98	4·0	2·64	4·43	6·80	..	..*
392·3	5·98	4·0	2·64	5·26	..	..	..*

* Uranium got precipitated due to hydrolysis.

TABLE II

Effect of pH on the separation of uranium from iron

U_3O_8 mg.	Initial pH of the solution	pH after H_2O_2 addition	pH adjusted by ammonia for precipitating complex	U_3O_8 in the precipitate mg.	Remarks
392·3	5·06	5·1	5·14	..	Precipitation incomplete even on long standing
392·3	5·06	5·16	5·66	..	Precipitation incomplete
392·3	5·06	5·13	6·02	391·8	
392·3	5·06	5·16	6·52	392·5	
392·3	5·06	5·16	6·74	395·1	Values are high due to precipitation of iron
392·3	5·06	5·14	6·86	396·5	Values are high due to precipitation of iron

TABLE III

U_3O_8 mg.	ThO_2 mg.	Oxides of rare earths mg.	Fe_2O_3 mg.	Concentration of U_3O_8 in solution gm./litre	Ratio of U_3O_8/ThO_2 + R.E. oxides	Ratio of U_3O_8/Fe_2O_3	U_3O_8 recovered mg.
391·2	5·98	4·0	2·4	4·77	39·2	163·0	389·0
391·2	11·96	8·0	4·8	4·68	19·6	81·5	390·2
391·2	23·92	16·0	9·6	4·45	9·8	40·8	389·8
391·2	47·84	32·0	19·2	4·07	4·9	20·4	392·0
195·6	119·6	80·0	19·2	2·45	0·98	10·2	197·0
97·8	119·6	80·0	19·2	1·63	0·49	5·1	97·4
48·9	299·0	200·0	48·9	0·45	0·098	1·0	48·2

following result: U_3O_8 99·9%; Fe_2O_3 0·090%; SiO_2 0·018%; Rare earth oxides + ThO_2 < 0·05%.

CONCLUSIONS

(1) Uranium is separated from thorium and rare earths from solutions containing as little as 0·45 g. U_3O_8/litre and U_3O_8/ThO_2 + Rare earth oxides = 0·1 if the pH of the solution before adding KF or NH_4F is about 3, or less.

(2) Uranium is separated from iron in the pH range of 6 to 6·5 in solutions containing 0·45 g. U_3O_8/litre and $U_3O_8/Fe_2O_3 = 1·0$.

(3) Complete separation of iron from uranium is achieved only after washing the peroxy complex of uranium with a large volume of water.

Fuller details of the method will be published elsewhere.

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STUDIES ON INDIAN PLANT GUMS: COMPOSITION AND GRADED HYDROLYSIS OF GUM KARAYA (*STERCULIA URENS* ROXB.)

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Gum karaya or Indian tragacanth is obtained from *Sterculia urens* Roxb. But the term is sometimes erroneously applied to the gum from *Cochlospermum gossypium* Kunth.[1] The gum is chiefly obtained from the deciduous forests of Northern and Central India, and finds extensive use in the textile, food and other industries; in fact it is a good substitute for gum tragacanth. In spite of its commercial importance and abundant availability, its chemistry does not seem to have been studied in any detail; only its physical properties have been recorded.[2] Hirst and co-workers have, however, referred to this gum as unpublished work in their publications on *Cochlospermum gossypium*[1] and *Sterculia setigera*,[3] which appeared a few years ago, but so far there has been no communication on the subject. As part of our investigations on Indian gums, the study of the gum from *Sterculia urens* has been carried out.

The material used in the present investigations was obtained from Madhya Pradesh. The impure gum occurs as the acetylated polysaccharide (acetyl content 6·72%; *cf. S. setigera* which contains 15·5%[3]). It was purified by precipitation from alkaline solution by means of acidified alcohol. During the course of this purification it gets deacetylated (*cf. S. setigera*[3]). Qualitative paper chromatographic analysis of the products of complete hydrolysis of the pure gum showed that only D-galactose, L-rhamnose and D-galacturonic acid were present. These were confirmed by the formation of suitable derivatives. It may be noted that in the related species, *S. setigera*, the gum has been found to contain D-tagatose also[3]; but in *S. urens* gum this ketose sugar could not be detected. The relative proportion of L-rhamnose and D-galactose was estimated by separating the two sugars on paper chromatogram and determining each sugar separately by alkaline oxidation with iodine,[4] and it was found to be 2:3. The uronic acid was estimated by the method of Dickson *et al.*[5] and it was 37·35 %. On this basis the composition of karaya gum works out to be L-rhamnose, D-galactose and D-galacturonic acid, present in the molecular proportion of 4:6:5.

The partial hydrolysis of the gum was brought about by refluxing with 5% sulphuric acid for 150 minutes. The " aldobiuronic " acid portion was isolated as the barium salt. On complete hydrolysis the " aldobiuronic " acid gave rise to L-rhamnose, D-galactose and D-galacturonic acid, and its equivalent weight was found to be 337, indicating that it was an equimolecular mixture of two aldobiuronic acids composed of D-galacturonic acid and L-rhamnose on the one hand and the same acid and D-galactose on the other. If it were an aldotriuronic acid composed of L-rhamnose, D-galactose and D-galacturonic acid, the equivalent weight would have been 488.

A majority of the gums yield only one aldobiuronic acid on graded hydrolysis and the formation of two acids in *S. urens* gum leads to the suspicion that the original material might be a mixture of two closely allied polysaccharides but the gum did not appear to be heterogeneous. Further, there are a number of cases where two aldobiuronic acids have been indicated.[1, 3, 6–10] The occurrence of two aldobiuronic acids, therefore, seems to be more common than expected in the past.

Experimental

The gum used in the present investigation was in the form of pale yellow lumps, each weighing from 2 g. to 5 g. Its proximate analysis was carried out in the usual manner. Moisture, fat, fibre, ash and proteinous matter were estimated according to standard methods.[11] The uronic acid was determined according to the method of Dickson, Otterson and Link[5] by noting the amount of carbon dioxide liberated on boiling with 12% hydrochloric acid. The acetyl group determination was carried out by refluxing the gum in presence of absolute alcohol with *p*-toluene sulphonic acid and determining the amount of ethyl acetate so liberated.[12] The following results were obtained:—Moisture 16·84%, ash 5·92%, proteinous matter 0·63%, fat 0·28%, crude fibre 0·41%, acetyl group 6·72% and uronic acid 31·91%.

Purification of the Gum.—The powdered gum (80 mesh, 40 g.) was added slowly to 2 litres of water containing 40 g. of sodium hydroxide, and stirred well by means of an electric stirrer. The material gradually, but only partially, dissolved, and after 6 hours it formed a viscous brown mass. The mixture was carefully acidified with concentrated hydrochloric acid and then treated with 6 litres of alcohol, when the gum was precipitated as a pinkish stringy solid. After decanting off the supernatant liquid, the gum was squeezed in a cloth, broken up into small bits and again taken in 2 litres

of water containing 10 g. of sodium hydroxide, with continuous stirring for six hours as before. The solution, which was pale yellow and mucilaginous, was quite homogeneous now. It was centrifuged in order to remove the suspended impurities and from the centrifugate the gum was precipitated as before. The operations of dissolution, centrifuging and precipitation were repeated twice again when the gum was obtained in a pure state. It was then dried, first in air and then in an electric oven, kept at 50° C., for 24 hours and powdered. Yield: 25 g. The purified gum (obtained after the 4th precipitation) was pinkish white in colour and was somewhat hygroscopic, but was not freely soluble in water. It analysed as follows:— Ash 0·49%, uronic acid 37·35%, acetyl grouping nil, and $[\alpha]_D^{20}$ (in N-sodium hydroxide) + 53·21°.

Complete Hydrolysis of the Gum.—After a number of preliminary experiments it was found that boiling the gum mildly under reflux with 5% sulphuric acid for 18 hours, taking 100 c.c. of the acid for every 5 g. of the gum, effected complete hydrolysis satisfactorily. The acid hydrolysate was neutralised with barium hydroxide using phenolphthalein as indicator. The precipitated barium sulphate was filtered off and the excess barium hydroxide was destroyed by the passage of carbon dioxide. After concentration to a small bulk (50 c.c.) in the presence of a little barium carbonate, the clear filtrate was treated with excess of alcohol (150 c.c.), when the barium salt of the uronic acid got precipitated. After leaving overnight the precipitated barium uronate was filtered and washed well with 70% alcohol in order to remove the adhering sugars. From the filtrate and the washings alcohol was distilled off and the volume made up to 200 c.c. The solution was analysed qualitatively and also quantitatively by paper chromatography for the constituent sugars. The barium uronate was purified by repeated precipitations from aqueous solution by means of alcohol. When macerated with hot methanol, it became quite crisp. This was examined separately.

Paper Chromatographic Examination of Sugar Solution.—Circular paper chromatography (method of Rao and Beri[13]) was used. Only D-galactose and L-rhamnose were detected and were confirmed by running mixed chromatograms by the method of Rao and Dickey.[14] The presence of D-galactose was further confirmed by the formation of mucic acid, m.p. 212° C., while the identity of L-rhamnose was confirmed by the formation of benzoyl hydrazone,[15] m.p. and mixed m.p. 180° C.

Quantitative Estimation of Sugars by Paper Chromatography.—The sugars were separated on filter-paper strips, using the solvent-descending

method,[16] extracted with water and finally estimated by oxidation with 0·1 N iodine solution in the presence of sodium carbonate-sodium bicarbonate buffer.[4] The sugars (L-rhamnose and D-galactose) were found to be in the molecular proportion of 2:3. The mixed sugar solution showed $[\alpha]_D^{20} = +51{\cdot}21°$ and this was in agreement with the above proportion of the sugars.

Identification of the Barium Uronate.—The barium salt of the uronic acid when examined by circular paper chromatography was found to be barium galacturonate.[17] Confirming this, an aqueous solution of the substance showed $[\alpha]_D^{20} = +24{\cdot}9°$ (barium galacturonate has $[\alpha]_D = +25{\cdot}1°$[18]), gave the characteristic brick-red precipitate with basic lead acetate[19] and on oxidation with nitric acid produced mucic acid, m.p. and mixed m.p. 212°.

Relative Proportion of the Constituent Sugars and Uronic Acid.—Uronic acid as already stated forms 37·35% of the gum. Hence the sugars constitute 62·65%. Since L-rhamnose and D-galactose are present in the molecular proportion of 2:3, the amount of L-rhamnose and D-galactose present works out to be 22·38% and 48·27% respectively. On the basis of this composition, L-rhamnose, D-galactose and D-galacturonic acid seem to be present in the gum molecule in the molecular ratio of 4:6:5.

Isolation of the "Aldobiuronic" Acid.—The purified gum (5 g.) was mildly boiled under reflux with 5% sulphuric acid (100 c.c.) with vigorous shaking to facilitate a rapid dissolution of the gum. In about 20 minutes the gum dissolved but the solution was somewhat turbid. It was, therefore, boiled for a while with a small amount of animal charcoal and filtered under suction. With the clear filtrate the boiling was continued. The course of hydrolysis was followed by a determination of the optical rotation at intervals of time. The rotation, when taken in a 10 cm. tube, assumed a constant value of +3·91° after boiling for about 120 minutes. After continuing the heating a little longer (150 minutes in all), the hydrolysate was cooled and then neutralised with barium hydroxide using phenolphthalein as indicator. The barium salt of the "aldobiuronic" acid was isolated in the usual manner by concentrating the neutralised hydrolysate to a small bulk and adding excess of alcohol. The precipitated salt was purified by repeated precipitations from aqueous solution by means of alcohol. After the 4th precipitation the substance was macerated with hot absolute methanol when it was obtained as a crisp powder. It was dried at 50° C. in an air-oven and finally in a vacuum desiccator at room temperature. Yield: 2·3 g. (Found: Ba, 16·68; uronic acid grouping, 47·94; an equimolecular mixture of the barium salts of D-galacturonosyl-D-

galactose, $C_{24}H_{38}O_{24}Ba$, and D-galacturonosyl-L-rhamnose, $C_{24}H_{38}O_{22}Ba$, requires Ba, 16·53; uronic acid grouping, 46·68%). In aqueous solution its specific rotation was found to be $+66·34°$ (C = 1%). From the aqueous solution the barium ion was carefully and exactly precipitated by means of dilute sulphuric acid and then the specific rotation of the aldobiuronic acid mixture was determined. It was found to be $+81·62°$ (C = 0·83%). The equivalent weight of the acid was determined by two methods: (1) from the barium content and (2) from the amount of carbon dioxide liberated when boiled with 12% hydrochloric acid and the two values obtained were respectively 344·2 and 337. The acid mixture underwent complete hydrolysis on boiling under reflux with 5% sulphuric acid for 18 hours and the hydrolysate contained L-rhamnose, D-galactose and D-galacturonic acid.

SUMMARY

Gum karaya (*Sterculia urens* Roxb.) is constituted from L-rhamnose, D-galactose and D-galacturonic acid which appear to be present in the molecular ratio of 4:6:5. D-tagatose, which has been reported to be present in other Sterculia gums, could not be detected in the sample of the karaya gum now examined. The original crude gum contains some acetyl groups also, which get detached during purification.

On graded hydrolysis with dilute sulphuric acid under controlled conditions, the gum yields L-rhamnose, D-galactose and a mixture of two aldobiuronic acids.

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CARRIER-FREE SEPARATION OF Sn^{113} FROM INDIUM

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Abstract

A procedure for the separation of carrier-free Sn^{113} from deuteron bombarded indium is described. The method employed depends on the extraction of stannic cupferrate from mineral acid solution using carbon tetrachloride, followed by ignition of the complex.

Introduction

Cupferron (ammonium salt of nitrosophenyl hydroxylamine) is now a well known reagent for metals, and has been extensively studied.[1, 2] It is of particular use since many of the complexes formed can be extracted with an organic solvent.

Mathers and Prichard[3] have used it in the separation of iron from indium in acid media and note that tin is one of the interfering metals. This iron-cupferrate complex can be selectively extracted with chloroform.[2]

Tin has been estimated by precipitation with cupferron and careful ignition to SnO_2 by Furman,[4] Pinkus[5] and Kling *et al.*[6] Mack and Hecht[7] have used cupferron for the separation of tin from antimony in hydrochloric acid solution.

It, therefore, seemed likely that a procedure for the separation of tin from indium using cupferron could be worked out. Earlier separations of tin from fission products involve the addition of carrier and precipitation from acid solutions to obviate the precipitation of indium.[8]

Experimental

The indium metal is melted off the target received from Birmingham University. A single channel spectrum of this metal shows peaks at 190 kev., 552 kev., 722 kev. and 1270 kev., ascribed to indium and one at 393 kev., due to Sn^{113}.

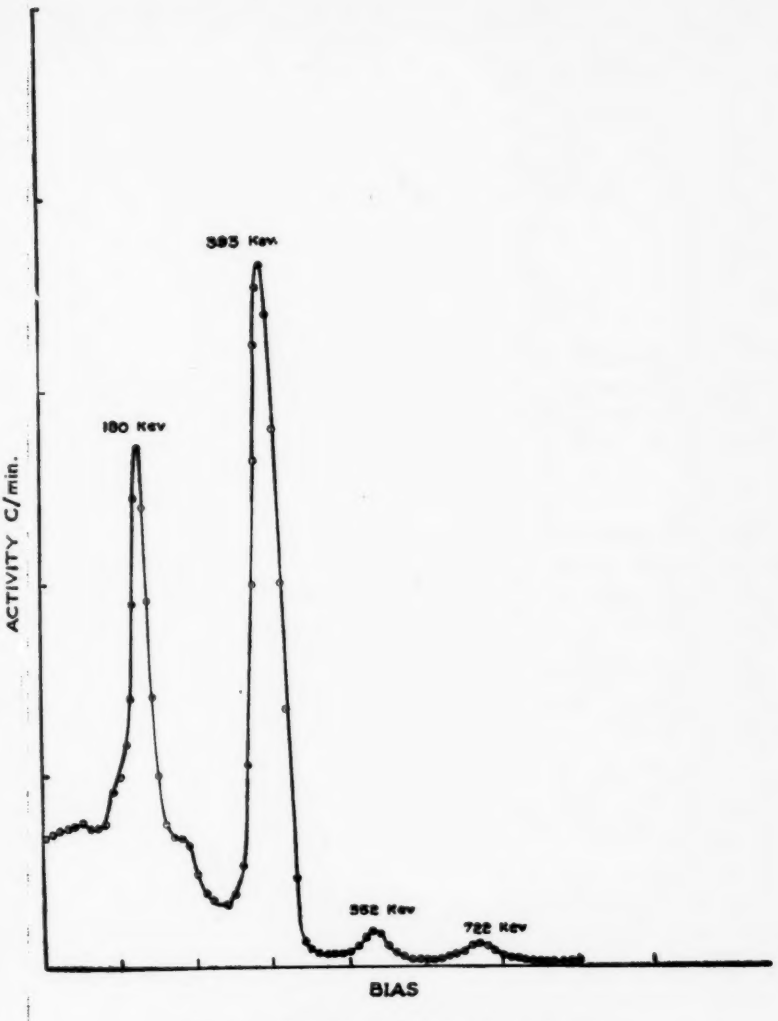

FIG. 1. Spectrum of In^{114}–Sn^{113} before Separation.

The metal was dissolved in 6 N HCl and the solution oxidised using bromine. Complete removal of the excess bromine was ensured by boiling.

About 10 c.c. of this oxidised solution giving around 10^5 counts per minute is treated with 10 c.c. of a fresh five per cent. solution of cupferron in

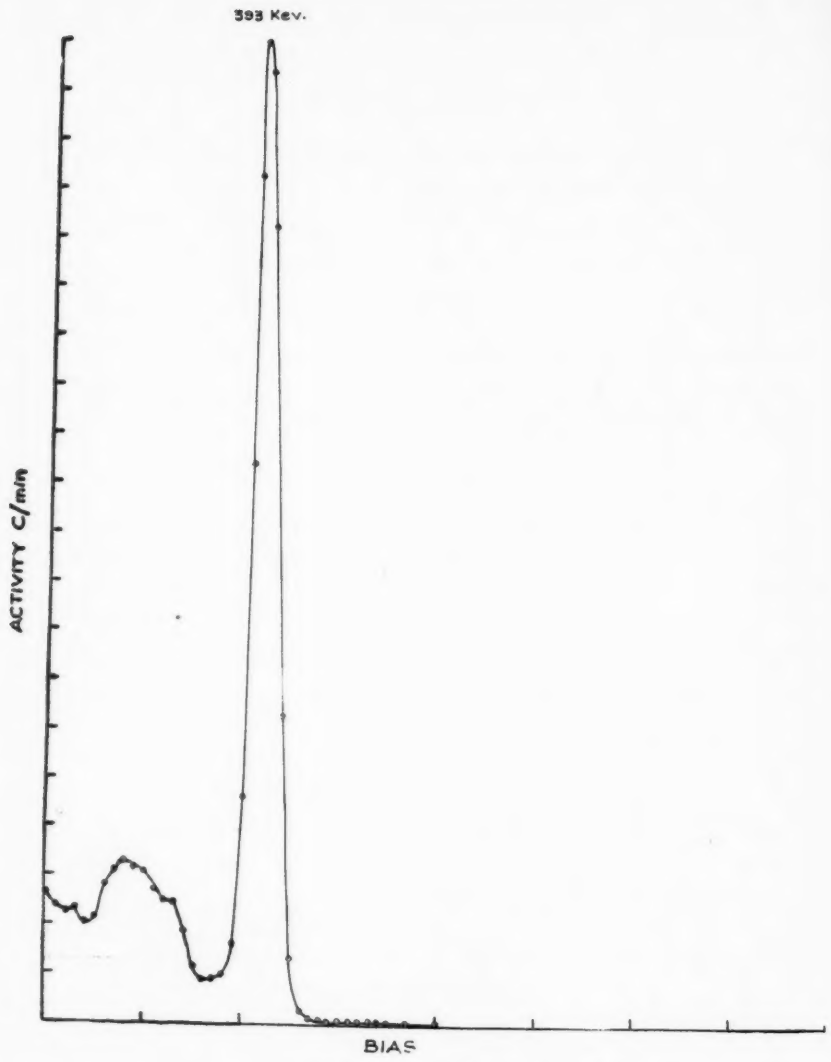

FIG. 2. Spectrum of Extracted Sn^{113}.

water. The final acidity is thus around 3 N. The solution is extracted twice with 20 c.c. of (Merck-Analar) carbon tetrachloride. The extracts are combined, evaporated and carefully ignited. The active residue of Sn^{113}

is then removed with a small amount of 2 N HCl, evaporated on a source holder and counted.

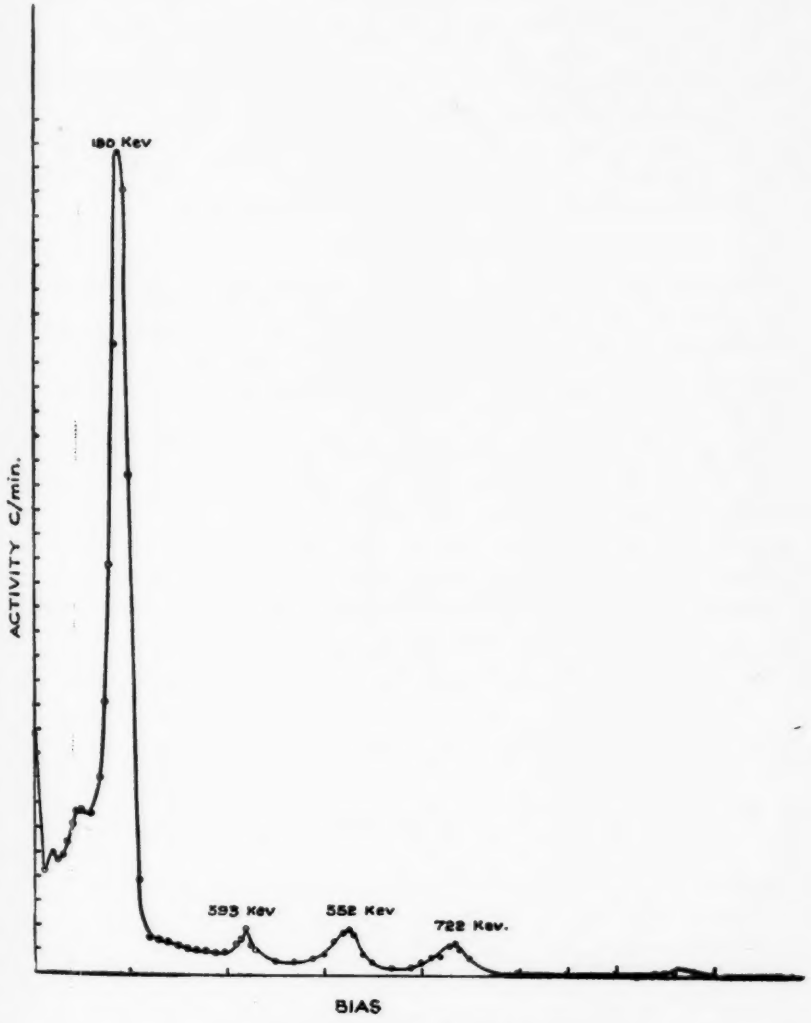

FIG. 3. Spectrum of In^{114} after Separation.

The separation has been followed by taking single channel spectra of the carbon tetrachloride extracts, the aqueous layer and the final source,

using a two-inch NaI (Tl) crystal. The results, shown graphically in Figs. 1 to 3, indicate almost complete removal of Sn^{113}, giving a clean carrier-free source.

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ON CERTAIN BS-REPRESENTATIONS AND A CHARACTERIZATION OF COMPLETE BOOLEAN ALGEBRAS

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Introduction

A BS-(or Birkhoff Stone) representation $a \to \mathcal{F}(a)$ of a lattice L is a homomorphism of L for finite meets (or lattice products) onto a family subsets of a fixed family $\mathcal{F} = \{I_\alpha\}$ of α-ideals[1] I_α of L, by which each element a in L is mapped on the subfamily $\mathcal{F}(a)$ of $\mathcal{F}$ comprising the I_α's containing a. The BS-representation $a \to \mathcal{F}(a)$ is said to be *isomorphic* if it is $(1-1)$ $\big(\mathcal{F}(a) = \mathcal{F}(b) \to a = b\big)$. It is said to *preserve arbitrary joins* if $\mathcal{F}(\bigvee_i a_i) = \bigvee_i \mathcal{F}(a_i)$ whenever $\bigvee_i a_i$ exists in L; (and dually arbitrary meets). The following results have been established by Birkhoff and Frink [4, Theorems 10 and 11].

Lemma I. *Let $a \to \mathcal{F}(a)$ be a BS-representation of L by subsets of $\mathcal{F} = \{I_\alpha\}$. Then*

(i) *$a \to \mathcal{F}(a)$ is isomorphic, if and only if, $\mathcal{F}$ separates L* (i.e., *to any two distinct elements of L there can be found in $\mathcal{F}$ an I_α containing one of them but not the other*);

(ii) *$a \to \mathcal{F}(a)$ preserves arbitrary joins, if and only if, each I_α in $\mathcal{F}$ is completely prime*[2];

(iii) *$a \to \mathcal{F}(a)$ preserves arbitrary meets, if and only if, each I_α is complete.*[3]

These conditions for the existence of isomorphic BS-representations preserving arbitrary joins or meets are expressed in terms of the structure of the

[1] The terms α-ideal and μ-ideal will be used, after Stone [7] for dual ideal and ideal (as defined in [5, p. 21]).

[2] An α-ideal I_α is called completely prime if always, $\bigvee_i a_i$ exists and $\bigvee_i a_i \in I_\alpha \to$ some $a_i \in I_\alpha$ (and dually for a μ-ideal I_μ).

[3] An α-ideal I_α is called complete if always, $a_i \in I_\alpha$ and $\bigvee_i a_i$ exists $\to \bigvee_i a_i \in I_\alpha$ (and dually for I_μ).

chosen family $\mathcal{F}$ of α-ideals of L. In the case of complete lattices it is shown here, that the conditions for existence of ismorphic BS-representations preserving arbitrary joins, or arbitrary meets can be put in terms of existence of special join, or meet basis (Definition 2) for L. In either case L has to have all joins distributive. For incomplete lattices with all existing joins distributive, conditions for the existence of isomorphic BS-representation preserving arbitrary joins is obtained in terms of existence of a meet basis of meet primes (Definition 1), for the elements of L considered as imbedded in the canonical extension of L for distributive joins. A parallel extension for the other result on the existence of isomorphic BS-representations preserving arbitrary joins and meets is shown to be true only partially (*vide* Theorem 4 and Counterexample 2).

Finally, as an application of the results, it is deduced that a complete atomic Boolean algebra can be characterized as a complete lattice with $\Pi_\alpha = 0_\alpha$ (*i.e.*, 1 is the sole element with meet complement 0) for which an isomorphic BS-representation exists preserving arbitrary joins; or equivalently, a complete lattice with $\Pi_\alpha = 0_\alpha$, having a meet basis of meet primes.

The author wishes to express his thanks to Dr. V. S. Krishnan for suggesting the extension of Theorem 1 to the non-complete case (Theorem 3) and also for help in shaping the final draft.

1. THE CASE OF THE COMPLETE LATTICE

Definition 1.—An element p of a lattice L not (necessarily complete) is called

(i) meet prime or *m.prime* if $a \frown b \leqq p \rightarrow a$ or $b \leqq p$,

(ii) join prime or *j. prime* if $a \smile b \geqq p \rightarrow a$ or $b \geqq p$,

(iii) completely meet prime or *c.m.prime* if (for all existing meets $\frown_i a_i$) $\frown_i a_i \leqq p \rightarrow$ some $a_i \leqq p$,

(iv) completely join prime or *c.j.prime* if (for all existing joins $\smile_i a_i$) $\smile_i a_i \geqq p \rightarrow$ some $a_i \geqq p$.

Clearly a prime α- or μ-ideal (in the usual sense [5, p. 141]) is a m.prime element of L_α (lattice of α-ideals of L) or L_μ. Again "p is a m.prime [j.prime] element" is equivalent to "principal μ-ideal $P_\mu(p)$ [α-ideal $P_\alpha(p)$] is prime"; and similarly "p is a c.m.prime [c.j.prime] element" is the same as "$P_\mu(p)$ [$P_\alpha(p)$] is completely prime (in the sense of Footnote 1)" (*cf.* [4, Theorem 17]). (Here $P_\mu(p)$ [$P\alpha(p)$] is defined by:

$$P_\mu(p) = \{x : x \leqq p\}\ [P_\alpha(p) = \{x : x \geqq p\}]).$$

Definition 2.—A subset S of L is called a *m.basis* (meet basis) or a *j.basis* (join basis) according as every element of L is expressible as a meet or join of elements from S.

Definition 3.—Given a family $\mathscr{F} = \{I_\alpha\}$ of α-ideals [$\{I_\mu\}$ of μ-ideals] of a lattice L and a subset L_0 of L, $\mathscr{F}$ is called a *separating* family over L_0, or said to *separate* L_0, if for any pair of distinct elements of L_0 there exists an I_α [I_μ] containing one of them but not the other.

The following lemmas relate to separability of L_0 by a family $\mathscr{F}$ of α-ideals of L.

LEMMA 2. *Over a subset L_0 of L, closed for finite meets, the family $\mathscr{F} = \{I_\alpha\}$ of α-ideals I_α is a separating family, if and only if, either of the two following equivalent conditions holds*:

(i) *for any a, b in L_0 with $a < b$, there is an I_α containing b but not a;*

(ii) *for any a, b in L_0 with $b \not\leqq a$, there is an I_α containing b but not a.*

Proof.—If $\mathscr{F}$ separates L, evidently (i) holds. Conversely, let (i) hold and a, b be any two elements in L_0 with $a \neq b$, so that $a \frown b < a$ or b, and $a \frown b$ is in L_0 (by hypothesis). Assume $a \frown b < a$, then by (i) there exists an I_α containing a but not $a \frown b$ (and hence also not b, since I_α is an α-ideal). That is, $\mathscr{F}$ separates L_0.

Next, obviously (ii) implies (i) since $a < b \rightarrow b \not\leqq a$). On the other hand, if (i) holds and $b \not\leqq a$, then $a \frown b < b$, so that by (i) there is an I_α containing b but not $a \frown b$ (and so also not a). Thus (i) implies (ii).

LEMMA 3. *Let L_0 be a subset of L, closed for finite meets and satsifying the condition: whenever $a^* \in L$, $a \in L_0$, and $a^* < a$, there exists $b \in L_0$ with $a^* \leqq b < a$. Then $\mathscr{F} = \{I_\alpha\}$ is a separating family over L, if and only if, each principal α-ideal $P_\alpha(a)$ of L, where $a \in L_0$, is the meet $\frown I_\alpha$ of the I_α's (in $\mathscr{F}$) containing a.*

Proof.—The "if" part is trivial. For proving the "only if" part, assume that $\mathscr{F}$ separates L_0. If possible suppose that $b^* \in \frown I_\alpha$ and $b^* (\notin P_\alpha(a))$; then $a \frown b^* < a$. Also $a \frown b^* \in \frown I_\alpha$ (since a, $b^* \in \frown I_\alpha$). By hypothesis on L_0, there exists an element $b \in L_0$ with $a \frown b \leqq b < a$. Since $\mathscr{F}$ separates L_0, there exists (by Lemma 2) an I_α containing a but not b. But b lies in $\frown I_\alpha$ (since $a \frown b \in \frown I_\alpha$ and $b \geqq a \frown b$). This contradicts the definition of $\frown I_\alpha$, whence $b^* \in P_\alpha(a)$. so that $\frown I_\alpha \subseteq P_\alpha(a)$; hence $\frown I_\alpha = P_\alpha(a)$ (since $a \in \frown I_\alpha$).

Remark 1.—The statement of the duals of Lemmas 2 and 3 (for a separating family of μ-ideals) is clear (the various inequalities have merely to be reversed).

Also, it is to be noted that the above lemmas (or their duals) are in particular valid for $L_0 = L$.

The following known facts repeatedly recur in the proofs below:

LEMMA 4. *(i) An α-ideal I_α of a lattice L is completely prime (complete and prime), if and only if, its complement $I_\mu = c(I_\alpha)$ is a complete and prime (completely prime) μ-ideal.*

(ii) Every principal α- or μ-ideal is complete; and conversely, in a complete lattice every complete α- or μ-ideal is principal.

The first statement follows easily from the definitions of completely prime, and complete ideals (*vide Footnotes* 1 and 2) by using the well-known result: complements of prime ideals are again prime ideals [7, Theorem 4]; while the second is an immediate consequence of the definitions of principal, and complete ideals.

The main results of the section can be now established.

THEOREM 1. *The following conditions on a complete lattice L are equivalent:—*

(i) *L has an isomorphic BS-representation preserving arbitrary joins;*

(ii) *there exists a family $\mathfrak{F} = \{I_\alpha\}$ of completely prime α-ideals I_α separating L;*

(iii) *L has a m.basis $\{p\}$ of m.prime elements p.*

Proof.—The equivalence of (i) and (ii) is given by Lemma 1 ((i), (ii)).

Next, let (ii) hold. By Lemma 4, since L is complete, $c(I_\alpha)$ is a principal, prime μ-ideal, $c(I_\alpha) = P_\mu(p)$, so that p is a m.prime element. The family $\mathfrak{F}' = \{P_\mu(p)\}$ also separates L (since this is true of $\mathfrak{F}$). Hence by the dual of Lemma 3 (with $L_0 = L$), $P_\mu(a) = \frown P_\mu(p)$ or, $a = \frown p$. That is, (iii) holds, whence (ii) implies (iii).

Now, suppose that (iii) holds. Then, if $a \neq b$, there is clearly a p with either $p \geqq a$, $p \geqq b$ or $p \geqq b$, $p \geqq a$. Hence $\mathfrak{F}' = \{P_\mu(p)\}$ is a separating family of μ-ideals over L. Since p is m.prime, $P_\mu(p)$ is prime, and consequently by Lemma 4, $I_\alpha = c(P_\mu(p))$ is completely prime. Also, $\mathfrak{F} = \{I_\alpha\}$ separates L. Thus (iii) implies (ii), and the proof is complete.

Remark 2.—Note that in the proof of the above theorem, completeness of L was required only to show (ii) implies (iii).

Hence in particular, (iii) implies (i) even when L is not complete. Also, when (iii) holds, L must have all (existing) joins distributive. For, then L has an isomorphic BS-representation preserving arbitrary joins (and finite meets); and since set unions are distributive the result follows. Thus

COROLLARY. *If L has a m.basis of m.prime elements, all (existing) joins in L are distributive.*

THEOREM 2. *The following conditions on a complete lattice L are equivalent*:

(i) *L has an isomorphic BS-representation preserving arbitrary joins and meets*;

(ii) *there exists a family $\mathcal{F} = \{I_\alpha\}$ of complete and completely prime α-ideals I_α separating L*;

(iii) *L has a j.basis $\{p'\}$ of c.j.prime elements*;

(iv) *L has a m.basis $\{p\}$ of c.m.prime elements.*

Proof.—The equivalence of (i) and (ii) follows immediately by combining the parts in Lemma 1. The proof will be now completed by showing that (a) (ii) and (iii) are equivalent (b) (ii) and (iv) are equivalent.

If (ii) holds, since I_α is complete and L is complete, I_α is principal; hence $I_\alpha = P_\alpha(p')$ where p' is a c.j.prime element (since I_α is also completely prime). Again, since $\mathcal{F}$ separates L, by Lemma 3 (with $L_0 = L$) it results: $P_\alpha(a) = \frown \mathrm{I}_\alpha = \frown P_\alpha(p') = P_\alpha(\smile p')$, or $a = \smile p'$. Therefore (iii) holds.

On the other hand, if (iii) holds, $a = \smile p'$ (p' being c.j.prime), and by reversing the above steps it follows that $P_\alpha(a) = \frown I_\alpha$ where $I_\alpha = P_\alpha(p')$ is a complete and completely prime α-ideal. Also, by Lemma 3, $\mathcal{F} = \{I_\alpha\}$ is a separating family over L. Hence (ii) holds and the proof of (a) is complete.

Finally, to prove (b) it suffices to remark that, in view of Lemma 4, (ii) can be equivalently rephrased as (ii′) there exists a family $\mathcal{F}' = \{I_\mu\}$, $\big(I_\mu = c(I_\alpha),\ I_\alpha = c(I_\mu)\big)$ of complete and completely prime μ-ideals separating L; (equivalence of (ii′) and (iv) follows, exactly as that of (ii) and (iii)).

Remark 3.—The part of this theorem asserting the equivalence of conditions (i) and (ii) is closely related to an earlier result of the author [2, Theorem 4].

Remark 4.—As in the previous theorem, the completeness of L is not required for proving (iii) implies (ii) (and also for the equivalence of (i) and (ii)).

2. THE CASE OF THE INCOMPLETE LATTICE

Throughout this section L will denote an incomplete lattice unless explicitly stated otherwise.

It has been established by MacNeille (*see* [6, Theorems 12·7–8]) that every lattice L (or even a half lattice) has a canonical extension L^* such that L^* is a complete lattice, and the imbedding $L \subseteq L^*$ preserves all *distributive* joins and *all* meets that exist in L. Moreover, the elements of L^* are distributive joins of elements of L. A join $\bigvee_i a_i$ (whenever it exists) is called distributive if $a \wedge (\bigvee_i a_i) = \bigvee_i (a \wedge a_i)$ for every $a \in L$ (*cf.* (6, Theorem 6.11)).

Consider next the relation between α-ideals of L and L^*. Each α-ideal I_α of L determines the *extension* $I_\alpha{}^*$, an α-ideal of L^*, consisting of all elements a^* of L^* with $a^* \geqq$ some $a \in I_\alpha$. And an α-ideal $I_\alpha{}^*$ of L^* determines the *section* by L, $I_\alpha{}^* \wedge L$ which is an α-ideal of L. Evidently, if $J_\alpha = I_\alpha{}^* \wedge L$, its extension $J_\alpha{}^* \subseteq I_\alpha{}^*$, while if J_α is the section $I_\alpha{}^* \wedge L$, of the extension $I_\alpha{}^*$ of I_α, $J_\alpha = I_\alpha$.

To extend Theorem 1 to the incomplete lattice case two lemmas are needed.

LEMMA 5. *If I_α is a completely prime α-ideal of L, its extension $I_\alpha{}^*$ is a completely prime α-ideal of L^*.*

Proof.—Let $\{a_i{}^*\}$ be a family of elements of L^* lying outside $I_\alpha{}^*$; then it has to be shown that their join $a^* = \overset{*}{\bigvee_i} a_i{}^*$ lies outside $I_\alpha{}^*$.

Recall now that every element of L^* is a distributive join of elements from L; hence, if $a_i{}^* = \overset{*}{\bigvee_j} a_{ij}$ $(a_{ij} \in L)$, $a^* = \overset{*}{\bigvee_i} a_i{}^* = \overset{*}{\bigvee_{i,j}} a_{ij}{}^*$, where all the joins are distributive. Were $a^* \in I_\alpha{}^*$, then $a^* \geqq$ some $a \in I_\alpha$. Hence $a = a \overset{*}{\wedge} a^* = a \overset{*}{\wedge} (\overset{*}{\bigvee_{i,j}} a_{ij}) = \overset{*}{\bigvee_{i,j}} (a \overset{*}{\wedge} a_{ij}) = \overset{*}{\bigvee_{i,j}} (a \wedge a_{ij})$, *i.e.*, $a = \overset{*}{\bigvee_{i,j}} (a \wedge a_{ij})$. Since a, $a \wedge a_{ij}$ are in L, and $L \subseteq L^*$, the last equation implies that $\bigvee_{i,j} (a \wedge a_{ij})$ exists and $a = \overset{*}{\bigvee_{i,j}} (a \wedge a_{ij}) = \bigvee_{i,j} (a \wedge a_{ij})$. But $a \in I_\alpha$ and I_α is completely prime, whence some $a \wedge a_{ij} \in I_\alpha$. Then, since $a_i{}^* \geqq a_{ij} \geqq a \wedge a_{ij}$, $a_i{}^* \in I_\alpha{}^*$—a contradiction. Hence $a^* \notin I_\alpha{}^*$ and the proof is complete.

LEMMA 6. *If I_α^* is a completely prime α-ideal of L^*, its section $J_\alpha = I_\alpha^* \frown L$ is a completely prime α-ideal of L provided, L has all existing joins distributive.*

Proof.—Since existing joins in L are distributive, the imbedding $L \subseteq L^*$ preserves all (existing) joins in L. Hence, if $\smile_i a_i \in I_\alpha \subseteq I_\alpha^* (a_i \in L)$, then $\overset{*}{\smile}_i a_i = \smile_i a_i \in I_\alpha^*$, whence by complete primality of I_α^*, some $a_i \in I_\alpha^*$; also $a_i \in L$. Hence $a_i \in I_\alpha^* \frown L = J_\alpha$. That is, J_α is completely prime, as was required to be shown.

The general form of Theorem 1 is now:

THEOREM 3. *The following conditions on a lattice L are equivalent:*

(i) *L has an isomorphic BS-representation preserving arbitrary joins;*

(ii) *there exists a family $\mathfrak{F} = \{I_\alpha\}$ of completely prime α-ideals in L which separates L;*

(iii) *every element of L is expressible as a meet of m.prime elements of L^*.*

Proof.—The equivalence of (i) and (ii) follows, as in Theorem 1, from Lemma 1 (which as already remarked does not depend on the completeness of L).

Next, assume that (ii) holds, and set $\mathfrak{F}^* = \{I_\alpha\}^*$ where I_α^* is the extension of I_α (in L^*). Then by Lemma 5, I_α^* are all completely prime α-ideals of L^*. Further, if $a < b$, and $I_\alpha \ni b$, $\ni a$, it is clear that $I_\alpha^* \ni b$, $\ni a$. Hence $\mathfrak{F}^*$ separates L ($\mathfrak{F}$ separates L by hypothesis). Write now $I_\mu^* = c(I_\alpha^*)$, then I_μ^* is prime and principal (Lemma 4) so that $I_\mu^* = P_\mu^*(p^*)$ with p^* m.prime (in L). Again $(\mathfrak{F}^*)' = \{I_\mu^*\}$ separates L (the same being true of $\mathfrak{F}^*$). Also, since elements of L^* are joins of elements of L, given $a^* \in L$, $a \in L \subseteq L^*$ and $a^* > a$, there can certainly be found a $b \in L$ with $a^* \geqq b > a$. Hence, by dual of Lemma 3, it results that for each principal ideal $P_\mu^*(a)$ $(a \in L)$, $P_\mu^*(a) = \overset{*}{\frown} I_\mu^* = \overset{*}{\frown} P_\mu^*(p^*)$, whence $a = \overset{*}{\frown} p^*$. So (iii) holds. Thus (ii) implies (iii).

Conversely, to prove (iii) implies (ii), assume now that (iii) is satisfied. Denote by $\{p^*\}$ the m.prime elements of L^*. Then $I_\mu^* = P_\mu^*(p^*)$ is prime, and $I_\alpha^* = c(I_\mu^*)$ is completely prime (Lemma 4). Since elements of L are meets of p^*'s $(\mathfrak{F}^*)' = \{I_\mu^*\}$ separates L, and hence $\mathfrak{F}^* = \{I_\alpha^*\}$ also

separates L. The section $I_\alpha = L \frown I_\alpha^*$ of I_α is completely prime (Lemma[4] 6), and if $\mathscr{F} = \{I_\alpha\}$, $\mathscr{F}$ separates L: for, if $a < b$, there is an $I_\alpha^* \supset b, \not\supset a$ (since $\mathscr{F}^*$ separates L) and then $I_\alpha = L \frown I_\alpha^* \supset b, \not\supset a$. Thus, $\mathscr{F}$ satisfies the requirements in (ii), and this completes the proof.

While the corresponding generalization for Theorem 2 is not completely true (*see* Counterexample 1), one can still prove the following:

THEOREM 4. *If L has distributive joins, and each element a of L is a join of c.j.prime elements of L^*, a is also a join of c.j.prime elements of L, and L has an isomorphic BS-representation preserving arbitrary joins and meets.*

Proof.—Observe first that a c.j.prime element c^* of L^* is necessarily an element of L. For, assume $c^* = \overset{*}{\underset{i}{\smile}} a_i$ $(a_i \in L)$ then $c^* = \text{some } a_i$, since c^* is c.j.prime. Next, c^* is a c.j.prime element of L since joins in L are preserved in L^* (if $\underset{i}{\smile} a_i \geqq c^*$, $\overset{*}{\underset{i}{\smile}} a_i = \underset{i}{\smile} a_i \geqq c^*$, whence some $a_i \geqq c^*$). Further, if $a = \overset{*}{\underset{i}{\smile}} c_i^*$, $a = \underset{i}{\smile} c_i^*$ (since $a,\ c_i^* \in L$ and $L \subseteq L^*$). Hence, the first part of the conclusion, and the second part results from the first (*see* Remark 4).

Next, it is convenient to establish

THEOREM 5. *In a Σ^+-sublattice L_1 of a direct union* [5, *p.* 25], $L = \Sigma_\lambda C_\lambda$ *of chains C_λ, there exists a separating family $\mathscr{F} = \{I_\alpha\}$ of completely prime α-ideals I_α, and hence (by Theorem* 3) *L_1 has an isomorphic BS-representation preserving arbitrary joins.*

A sublattice L_1 of a lattice L is said to be a *Σ^+-sublattice* if $a_i \in L_1$ and join $\overset{1}{\underset{i}{\smile}} a_i$ in L_1 exists, together imply join $\underset{i}{\smile} a_i$ in L_1 exists, and $\underset{i}{\smile} a_i = \overset{1}{\underset{i}{\smile}} a_i$, *i.e.*, L considered as an extension (in the sense of [6, p. 137]) of L_1 preserves all existing joins.

Proof.—Let $a = \{a^\lambda\}$ be any element in L_1. The set $I_\alpha = I_\alpha(a^\lambda)$ of all elements x in L_1 such that the λ-component of x, $x^\lambda > a^\lambda$, constitute a completely prime α-ideal of L_1. For, let $x_i \in L_1$ lie outside I_α, and $x = \overset{1}{\underset{i}{\smile}} x_i$

[4] That L has all existing joins distributive follows from hypothesis (iii). For let $\underset{i}{\smile} b_i$ be an existing join and a any element in L. Then clearly $c = a \frown (\underset{i}{\smile} b_i) \geq$ (each) $a \frown b_i$. If $t \geq a \frown b_i$, and $t = \underset{j}{\frown} p_j^*$—where p_j^* are m.primes of L^* then $p_j^* \geq t \geq a \frown b_i$. Hence $p_j^* \geq a$ or (all) b_i *i.e.*, $\geq c$. Therefore $t = \frown p_j^* \geqq c$, whence $\underset{i}{\smile} (a \frown b_i)$ exists and $= c$.

exist. Then $\bigvee_i x_i$ exists and $\bigvee_i x_i = x$ (by hypothesis on L_1). Since $x_i \in I_a$, $x_i^\lambda \leqq a^\lambda$; hence, the lattice operations being component-wise in L (as a direct union), $x^\lambda = (\bigvee_i x_i)^\lambda = \overset{\lambda}{\bigvee_i} x_i^\lambda \leqq a^\lambda$ ($\overset{\lambda}{\vee}$ denoting join in C^λ). Consequently x lies outside I_a.

Next, the family $\mathscr{F} = \{I_a\}$ of all I_a's (got by varying a and λ) separates L_1, since $a_1 > a_2$ implies $a_1^\lambda > a_2^\lambda$ (for some λ). Thus, the family $\mathscr{F}$ has the required properties and the theorem follows.

COROLLARY. *If L_1 in the above Theorem is complete, L_1 has a m.basis of m.prime elements* (*vide* Theorem 2).

Now two counterexamples will be furnished to show that (a) a lattice L may have an isomorphic BS-representation preserving arbitrary joins and meets, even when its extension L^* does not contain c.j.prime elements forming a j.basis for L (*cf.* Theorem 3), and (b) in condition (iii) of Theorem 3 one can assert, when L is not complete, only that every element of L is a meet of m.prime elements of L^* and not m.prime elements of L.

Counterexample 1.—L_0 consists of all rational numbers lying in the closed interval $L = [0, 1]$. L_0 and L are lattices (L complete) with respect to the usual order; also it is easy to see (and in fact well known) that L can be identified (*i.e.*, in the sense of isomorphism) with L_0^* (the canonical extension of L_0).

The intervals $I_a = I_a(i)$ of L_0 comprising all rationals in $[i, 0]$, where i is an irrational, are α-ideals—which are also easily verified to be complete and completely prime. Also $\mathscr{F} = \{I_a\}$ separates L_0. Hence L_0 has an isomorphic BS-representation preserving arbitrary joins and meets (Lemma 1). Since, however, each element $a \neq 0$ of L is the join of all elements $x < a$, a cannot be c.j.prime, and so the c.j.prime elements of L do not form a basis for L_0.

Counterexample 2.—L' is the direct union $L + L$, where $L = [0, 1]$; L_0' comprises all rational pairs (a^1, a^2) where $0 < a^1 < 1$, $0 < a^2 < 1$, together with (0, 0) and 1, 1). L_0' is easily seen to be a Σ^+-sublattice of L', and consequently by Theorem 5, L_0' has an isomorphic BS-representation preserving arbitrary joins. Nevertheless, no element (except (1, 1)) of L_0' is m.prime. For, if $(a^1, a^2) \neq (1, 1)$, $(a^1, a^2) = (a^1, b^2) \frown (b^1, a^2)$ where $a^1 < b^1 < 1$, $a^2 < b^2 < 1$. Thus, elements of L_0' cannot be expressed as meets of m.primes from L_0'. On the other hand, every element (a^1, a^2) of L_0' is a meet of m.primes from L—verifying the conclusion of Theorem 3, since $(a^1, a^2) = (a^1, 1) \frown (1, a^2)$ and $(a^1, 1)$, $(1, a^2)$ are (as easily shown) m.prime elements of L' (note, these elements do not lie in L_0').

3. A CHARACTERIZATION OF COMPLETE ATOMIC BOOLEAN ALGEBRAS

Definition 4.—In any lattice L with 0, the *meet complement* or m.complement[5] of an element a is defined as the largest element (if it exists) with the property $a \frown a' = 0$. Clearly an element a has m.complement 0, if and only if, it has the property: $a \frown x = 0 \rightarrow x = 0$ (for all $x \in L$). The set $\{a\}$ of elements $a \in L$ having 0 as m.complement is denoted by Π_a[6]; Π_a is easily seen to be an α-ideal (admitting the null-set also as an ideal) — (if a, $b \in \Pi_a$, then $a \frown b \in \Pi_a$ since $a \frown b \frown x = 0 \rightarrow b \frown x = 0 \rightarrow x = 0$).

If L contains the element 1, clearly $1 \in \Pi_a$; and if Π_a consists of solely the element 1, this will be expressed by writing $\Pi_a = 0_a$ $(= \{1\})$ — (0_a can be interpreted as the zero element of the lattice of non-null α-ideals of L).

In the sequel it will be supposed that L always contains 0 and 1.

An element M of L is called *maximal* if $M \neq 1$, and $x > M \rightarrow x = 1$; the dual of a maximal element is an *atom* or *minimal* element. The lattice L is called atomic if it has a j.basis of atoms (with 0).

LEMMA 7. *A maximal element M of a distributive lattice L is m.prime* (*cf.* [7, *Theorem* 3]); *a m.prime element $p \neq 1$ in a lattice L in which $\Pi_a = 0_a$, is maximal.*

Proof.—For the first part, let L be distributive and $M \geqq a \frown b$ then $M = M \smile (a \frown b) = (M \smile a) \frown (M \smile b)$ so that $M \smile a$ or $M \smile b \neq 1$, and hence $= M$ (since M is maximal). That is, a or $b \leqq M$, whence M is prime.

For the second part, assume that $\Pi_a = 0_a$ and $a > p$. If $a \frown x = 0$, then since $p \geqq a \frown x = 0$, $a \leqq p$, and p is prime, it results: $x \leqq p < a$ so that $x = a \frown x = 0$. Thus $a \in \Pi_a = 0_a$, and hence $a = 1$, or p is maximal.

THEOREM 6. *Among complete lattices for which $\Pi_a = 0_a$* (i.e., *consists of the sole element* 1), *the complete, atomic Boolean algebras are precisely those which have isomorphic BS-representations preserving arbitrary joins.*

Proof.—First, let L be a complete, atomic Boolean algebra; then L is complemented and hence $\Pi_a = 0_a$ (for, $a \smile a' = 1$, $a \frown a' = 0$, and $a \neq 1$ together imply $a' \neq 0$, or $a \in \Pi_a$). Further the complements m' of atoms m are maximal elements (as is well known) and since the atoms m (with 0) form a join basis for L, the maximals m' (with 1) form, as can be easily seen,

[5] Or pseudo-complement in the terminology of Birkhoff [5].

[6] The ideal Π_a was first considered by Vaidyanathaswamy, for a distributive lattice, in his paper [9].

a meet basis for L. Again by Lemma 7, since L is distributive the elements m' are prime. Thus $\{m'\}$ form a m.basis of m.primes for L, whence by Theorem 1, L has an isomorphic BS-representation preserving arbitrary joins.

Next, let L be a complete lattice with $\Pi_\alpha = 0_\alpha$, having such an isomorphic BS-representation. It is required to show that L is an atomic Boolean algebra. By Theorem 1, L has a m.basis $\{p\}$ of m.primes p, and so by the corollary (to Theorem 1) L has all joins distributive; hence L is closed for m.complements [5, p. 147, Theorem 15]. Therefore, since $\Pi_\alpha = 0$, L is a Boolean algebra (*vide* [1, Theorem 10]). Further, the m.primes p ($\neq 1$) are maximal (Lemma 7), and hence their complements p' are atoms; also the p' form a j.basis for L (since $\{p\}$ is a m.basis). That is L is atomic, and the proof is complete.

COROLLARY. *A complete, atomic Boolean algebra can be characterized as a lattice* L *with the properties*:—

(i) L *is complete ;*

(ii) L *has a m.basis of m.primes ;*

(iii) $\Pi_\alpha = 0_\alpha$.

Remark 5.—In [3] a related characterization for complete Boolean algebras (not necessarily atomic) has been given. Subsequent to the writing of this paper, the author has been able to establish the following modified form of Theorem 6 (which is free of the " completeness " assumption in the original):—

Among Boolean algebras (whether or not complete), the atomic Boolean algebras are precisely those that have isomorphic BS-representations preserving arbitrary joins. (The proof will appear elsewhere.)

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RAMAN EFFECT STUDIES IN CHELATION

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I. Introduction

The spectroscopic effects of internal hydrogen bonding or chelation were first observed by Wulf, Hendricks, Hilbert and Liddel (1935) in infrared absorption. They noticed that in a series of substances (including salicylaldehyde) which had an acceptor (OH) and a donor (C = O) group placed suitably on the molecule, the hydroxyl group does not show a strong absorption peak at 7000 cm.$^{-1}$ which is the first overtone of the OH stretching vibration. Other investigators like Errera and Mollet (1935), Bonino and Manzoni-Ansidei (1937) have observed the lowering of the carbonyl frequency in chelate compounds. The lowering of the hydroxyl and carbonyl frequencies were explained as arising out of the presence of a strong internal hydrogen bond between the two groups.

To determine the effects of environment on the prominent frequencies affected by chelation, solutions of chelate substances in various polar and non-polar solvents were investigated. Rolla (1940) studied the Raman spectrum of pure salicylaldehyde in methyl alcohol, benzene, cyclohexane and carbon tetrachloride. His results indicate that the carbonyl frequency of salicylaldehyde remains unaffected either by the solvent or its concentration. Puranik (1955) has reported an increase of the C = O frequency of salicylaldehyde in methyl alcohol mixtures. It was, therefore, decided to reinvestigate the effect of different types of environment on various types of chelate substances in an exhaustive way and the results obtained in the case of salicylaldehyde are given here.

II. Experimental

A Hilger Raman Source Unit and a Fuess Glass Spectrograph having a dispersion of 19 cm.$^{-1}$ per mm. in the λ 4358 A region were used in these experiments. The source enables an intense Raman picture of the substance to be recorded in a few minutes. Hartmann's diaphragm technique was employed to study the changes in frequency of the substance. The spectrum of the substance in solution is locked in between the spectra of the pure substance on either side. Thus, while a Raman line may itself have a

width of 4 or 5 cm.$^{-1}$, measurement of the positions of the edges of the shifted and unshifted lines by a comparator enable the relative changes of frequency to be determined in a narrower range.

III. Results and Discussion

Solutions of salicylaldehyde in phenol, orthocresol, alcohols (methyl, ethyl, *n*-propyl, *n*-butyl) and dioxane were studied. As Pauling (1940) has pointed out, the phenols are known to be capable of forming strong hydrogen bonds and are not highly associated. These two factors together make the hydrogen of the OH group of phenol a strong acceptor. The aliphatic alcohols, on the other hand, are known to be strongly associated substances offering donors and acceptors of roughly equal strength. Mizushima (1954) ranks, in the order of acceptor strengths, phenol sixth and methyl alcohol eleventh. In the order of donor strengths, phenol and methyl alcohol are ranked twenty-four and eighteen respectively. Dioxane is a non-polar liquid possessing a highly electronegative atom like oxygen and is known to offer donor groups only.

The complete Raman spectrum of salicylaldehyde as recorded by the author is given below:

149 (3*d*), 219 ($\frac{1}{2}$), 266 (3 *b*), 298 ($\frac{1}{2}$), 413 (3), 453 (7), 524 ($\frac{1}{2}$), 562 (7), 640 (1), 769 (12), 890 (1), 1030 (9), 1113 (2), 1151 (7), 1229 (11), 1279 (2), 1322 (9), 1381 (2), 1579 (9), 1619 (7), 1644 (8), 1667 (9), 3035 (1).

In the various mixtures, the carbonyl frequency of salicylaldehyde at 1667 is affected. To avoid repitition, results for environments of phenol, methyl alcohol and dioxane only are given below, since these three substances provide three different types of environments.

TABLE

Mixtures of salicylaldehyde with phenol, methyl alcohol and dioxane

No.	Mixtures with	C = O frequency				
		1 : 0	1 : 1	1 : 2	1 : 4	Average shift
1	Phenol ..	1667	1664	1664	1664	−3
2	Methyl alcohol ..	1667	1670	1671	1671	+4
3	Dioxane ..	1667	1669	1670	1670	+2·5

It is seen that the changes in the carbonyl frequency, whether positive or negative, produced by the different environment are very small. In

benzaldehyde-phenol mixtures, Puranik (1953) has recorded a decrease of the C = O frequency of the former at 1694; the amount of decrease is found to vary between 10 to 14 cm.$^{-1}$ depending on dilution. The salicylaldehyde-phenol mixtures from the above table show a decrease in the carbonyl frequency of about 3 cm.$^{-1}$ The difference between benzaldehyde and salicylaldehyde (*o*-hydroxy benzaldehyde) is the O–H group situated in the ortho-position to the aldehydic group, in the latter compound. This produces a chelate ring in salicylaldehyde and makes the molecule a sort of closed system where the hydrogen bonding capacities of the acceptor and donor groups are largely saturated by the internal hydrogen bond itself. Perturbation effects produced on chelate compounds by different environments can, therefore, be only of the second order and hence the smallness of the changes in frequency.

In salicylaldehyde, the oxygen of the carbonyl group is linked up internally to the hydrogen of the hydroxyl group; in a phenol environment, it appears to form an additional external hydrogen bond with the OH group of phenol which, as has been discussed earlier, is in a position to form strong hydrogen bonds and hence the reduction in the C = O frequency. Similar results have been obtained by Flett (1948) in hydroxy anthraquinones. Anthraquinone has an absorption band at 1675 attributable to the carbonyl linkage. Under the influence of one hydrogen bond, as in 1 : 4-dihydroxy anthraquinone, this frequency falls to 1630. In the case when each of the carbonyl oxygens forms two hydrogen bonds with two neighbouring hydroxyl groups as in 1 : 4 : 5 : 8-tetrahydroxy anthraquinone, the bonded C = O frequency falls to 1590. Identical results have been observed by Hadzi and Sheppard (1954) in the case of deuteroxy anthraquinones.

Methyl alcohol is seen to produce an increase in the carbonyl frequency of about 4 cm.$^{-1}$ In methyl alcohol-benzaldehyde mixtures, Puranik (1953) records a small decrease of the carbonyl frequency. As against benzaldehyde, having only a donor group, salicylaldehyde can offer both donor and acceptor groups. Hydrogen bonds are therefore possible between the carbonyl group of salicylaldehyde and the hydroxyl group of methyl alcohol. Such hydrogen bonds will have an effect of weakening the carbonyl link and of reducing its frequency. Hydrogen bonds are also possible between the hydroxyl group of salicylaldehyde and the hydroxyl group of methyl alcohol. Such hydrogen bonds, if formed, will have an effect of loosening the internal hydrogen bond and hence of increasing the carbonyl frequency. The change of frequency should be considered as a resultant of these two effects. Enhancement of carbonyl frequency seems to indicate that the loosening

of the internal hydrogen bond is decisive and preponderates over the weakening of the carbonyl link.

In the dioxane-salicylaldehyde mixtures, the C = O frequency is enhanced. Dioxane offers only a donor group and hydrogen bonds are likely to be formed between the oxygen of dioxane and the hydrogen of the OH group of salicylaldehyde. This appears to loosen the grip of the OH group on the C = O group, resulting in a small enhancement of the carbonyl frequency.

IV. SUMMARY

Salicylaldehyde is a substance having a carbonyl group and a hydroxyl group in neighbouring positions between which an internal hydrogen bond is known to exist. In environments of phenol, methyl alcohol and dioxane, these groups appear to form additional external hydrogen bonds. The effects of such bond formation are found to be very small, indicating that chelation is very strong in this substance.

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RAMAN EFFECT IN MIXTURES OF PYRIDINE WITH PHENOL, METHANOL, AND WATER

(N - - - H Hydrogen Bond Formation)

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I. INTRODUCTION

RAMAN effect has been extensively used to study the hydrogen bond formation with oxygen in carbonyl compounds. Koteswaram (1940) has studied the variation of the frequency due to the vibrations of C = O link in aqueous solutions of acetone. Murty and Seshadri (1941, 1942) have studied these variations in mixtures of aldehydes and esters with pehnol and methyl alcohol. Puranik (1953, 1955) has investigated the effect of environment on the frequencies of ketonic, aldehydic and ester groups when these groups are placed in the environments of acceptor solvents. He has suggested that the variations in different frequencies of carbonyl compounds in mixtures are not isolated in themselves, but they are the effects on the whole group, as the consequences of hydrogen bond formation.

The effects of N - - - H hydrogen bond formation have been observed experimentally only in infra-red absorption. Nelson Fuson *et al.* (1952) have recorded the NH - - - N hydrogen bonding in the absorption spectra of many compounds. Lakshmanan (1954) has investigated the effect of concentration on the Raman spectrum of mixtures of pyridine and fatty acids. He postulates the formation of pyridine-acid complexes, in view of the variation in intensity and structure of the Raman spectrum of pyridine in the mixture.

The manifestation of the N- - -H hydrogen bond formation by Raman spectroscopic methods has not been recorded in literature. With the advent of more powerful techniques of photographing intense Raman spectra, the lines can now be recorded within a few minutes. This has enabled the authors to study the finer features of the effects of N- - -H hydrogen bond formation, which are not as pronounced as those of O- - -H bond formation. With a view to study these effects pyridine was chosen, and detailed investigations on the mixtures of pyridine and acceptor solvents have been undertaken.

II. EXPERIMENTAL

Pyridine of high grade purity was procured, and distilled under reduced pressure. Phenol, methanol and water were purified by the conventional methods. Using the experimental technique described in an earlier communication by one of the authors (1953), an intense Raman spectrum of pyridine has been photographed in thirty minutes. With the decrease of the pyridine content of the mixtures, proportionally greater time is allowed for exposures so that Raman lines of comparable intensity could be photographed. In order to detect and measure the shifts of the order of a few wave numbers, the technique of Hartmann diaphragm was utilised. The spectrum of pure pyridine was photographed on the top and bottom, and the spectrum of the mixture was hemmed in between the spectra of pure pyridine (*see* Plate I).

III. RESULTS

The Raman frequencies of pyridine as recorded by the authors are given below:

373 ($\frac{1}{2}$), 402 ($\frac{1}{2}$), 602 (2), 651 (4), 887 (1), 933 (1), 990 (10), 1027 (10), 1066, ($\frac{1}{2}$) 1143 (2 *b*), 1178 (1), 1217 (5), 1257 ($\frac{1}{2}$), 1378 ($\frac{1}{2}$), 1478 (1), 1528 ($\frac{1}{2}$), 1578 (5 *b*), 1590 (1 *s*), 2916 (3), 2954 (3), 2998 (3), 3058 (8).

The frequencies substantially agree with those recorded by Kohlrausch and his co-workers.

Mixtures of pyridine with phenol, methanol and water under the concentrations of 1 : 1, 1 : 2, and 1 : 4 by volume have been studied. Mixtures of higher concentrations could not be investigated because of the critical opalescence setting in at those concentrations. The variations in the different frequencies of pyridine in mixtures of phenol, methanol and water for different concentrations, are given in Table I.

IV. ASSIGNMENT OF LINES

Taking into consideration the essential similarity between the structures of pyridine and benzene, Kline and Turkevitch (1944) and Corssin *et al.* (1953) have assigned most of the lines of pyridine to different modes of ring vibrations. Herzberg (1951) has described the different modes of ring vibrations of benzene and associated the different linkages in it to corresponding modes of vibrations. Drawing the analogy from benzene, the well-known frequencies like 602, 887, 1027, 1597 and 3054 cm.$^{-1}$ have been assigned to the vibrations of different linkages, as detailed in coloumn No. 2 of the Table I. The three lines 933, 1218 and 1578 cm.$^{-1}$ are left unassigned because they do not have their parallels in benzene. Due to the substitution of nitrogen in

TABLE I

Frequencies in mixtures of pyridine with acceptors

Sl. No.	Assignment	Frequency of pyridine ($cm.^{-1}$)	Pyridine-Phenol Mixtures			Pyridine-Methanol Mixtures			Pyridine-Water Mixtures		
			1 : 1	1 : 2	1 : 4	1 : 1	1 : 2	1 : 4	1 : 1	1 : 2	1 : 4
1	C—C—C (bending) ..	602	608	610	610	608	608	608	606	606	606
2	— ..	641	638	632	632	634	634	634	634	634	634
3	C—H⊥ .. (bending)	887	894	896	900	893	896	896	892	892	892
4	C—N .. (bending)	933	941	945	945	935	938	938	935	938	938
5	C—C .. (stretch)	990	995	1000	1000	993	998	998	994	1000	1000
6	C—H ‖ (bending) ..	1027	1027	1024	1024	Shows inclination to diminish			Shows inclination to diminish		
7	C—N .. (stretch)	1218	1214	1208	1208	1216	1215	1215	1216	1215	1215
8	— ..	1478	1483	1483	1483	1480	1482	1482	1482	1482	1485
9	C = N ..	1578	1586	1596	1596	1581	1585	1585	1581	1584	1584
10	C=C ..	1597	1590	1590	1590	1592	1592	1592	1592	1592	1592
11	— ..	2954	2960	2962	2966	2960	2965	2965	2960	2965	2965
12	C—H .. (stretch)	3054	3061	3061	3062	3062	3062	3062	3064	3064	3064

place of C—H in benzene the degeneracy present in benzene is released in pyridine. This has resulted in the splitting of the line at 1584 cm.$^{-1}$ in benzene, assigned to C = C of the ring, into two lines at 1578 and 1590 cm.$^{-1}$ in pyridine. Bellamy (1954) ascribes the line at 1578 cm.$^{-1}$ to the vibrations of C = N. The intensity considerations in benzene and pyridine support this assignment.

The line at 1218 cm.$^{-1}$ in the spectrum of pyridine has no counterpart in benzene. Therefore this can be assigned to the vibrations of C—N stretch in pyridine. This assignment finds its confirmation in the assignment of C—N bond made earlier by the authors (1956) in the case of *p*-tolyl isothiocyanate. The frequency thus assigned in the cyanate is 1241 cm.$^{-1}$, which is higher, probably because the C—N bond is outside the ring. Le Fevre *et al.* (1953) in their studies of the infra-red spectra of compounds containing the azo group have assigned the lines in the region of 1250 cm.$^{-1}$ to the C—N stretch. They have assigned the lines into the region of 930 cm.$^{-1}$ in azo compounds to the inplane bending vibrations of C—N = C. Therefore the line at 933 cm.$^{-1}$ in pyridine can be assigned to the in plane bending vibrations of C — N = C.

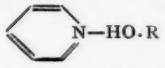
V. DISCUSSION OF RESULTS IN THE MIXTURES

By mixing pyridine with acceptor solvents like phenol, methanol and water, opportunities are created for the formation of hydrogen bonds between the nitrogen of pyridine and hydrogen of the solvent. The fact that hydrogen bonds are formed with the nitrogen of pyridine is proved by an auxilliary experiment of recording the Raman spectrum of the mixtures of pyridine with benzene and dioxane which are not acceptor solvents. In these mixtures none of the pyridine lines is affected, because of the lack of opportunities for the formation of the bond.

It is seen from Table I that twelve out of twenty-two frequencies of pyridine are affected due to the presence of acceptor molecules in the proximity of the molecules of pyridine (*see* Plate). Thus it appears that the whole ring is getting influenced because of the environment. In the earlier work on hydrogen bond formation with aldehydes, ketones and esters, it has been observed by one of the authors (1953) that the effect is prominent on the carbonyl frequencies, and there are secondary effects mainly on the adjoining links. The ring frequencies are seldom effected except in the case of anisaldehyde, in which the frequencies attributed to the vibrations of the ring get affected because of the presence of the methoxy group in the para position. In all such cases, where the ring frequencies remain unaffected, it is seen that the oxygen which is the direct participant in the hydrogen bond formation is

not a member of the ring. Probably this explains why the ring frequencies do not get affected, and whatever be the effects due to the realignment of the electronic distribution at the C = O end, they are spread only to the adjacent links outside the ring in a secondary way.

In the case of pyridine, nitrogen which is the participant in the hydrogen bond formation is a member of the ring. The effects due to hydrogen bond

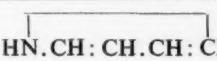
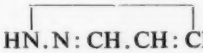
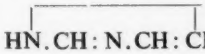
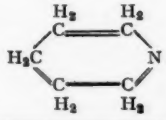


formation are directly introduced into the ring either by way of C — N or C = N which are adjacent linkages in the pyridine ring. Probably it is this induction of the effects of bond formation directly into the ring, that results in the variations of quite a large number of ring frequencies.

The behaviour of frequencies attributed to the modes of vibrations mainly associated with C — N or C = N appear to be dissimilar to that of C = O in the carbonyl compounds. In general the frequency attributed to C = O gets reduced in the mixtures of acceptor solvents. In the case of pyridine, the frequency attributed to the vibrations of C = N at 1578 cm.$^{-1}$ shows an enhancement in its magnitude to the maximum extent of 16 cm.$^{-1}$ The frequency at 1218 cm.$^{-1}$ associated with vibrations of the C — N bond is lowered to the maximum extent of 10 cm.$^{-1}$ These effects are not isolated in themselves, but appear to produce effects in varying degrees on the different frequencies associated with the vibrations of the pyridine ring.

TABLE II

The C — N frequencies in cm.$^{-1}$

Compound	Formula	Frequency	Author
1. Pyrrole ..		1144	B & A* (1933)
2. Pyrazole ..		1149	B & A* (1936)
3. Imidazole ..		1150	Kohlrausch & Seka (1938)
4. Piperdine ..		1146	Kohlrausch & Stockmair (1936)

* Bonino, G. B. and Manzoni Ansidei, R.

The C — N frequency is lowered by processes other than hydrogen formation, *e.g.*, chemical substitution, in some of the five-membered ring compounds such as pyrrole, pyrazole imidazol and six-membered ring compound like piperidine. The frequencies are given in Table II.

The large magnitude of the lowering of the frequencies is due to the chemical substitution. No comments can be offered on the frequencies in the above compounds in the region of 1550 cm.$^{-1}$, since such lines have not been recorded in their spectra.

P. Krishna Murti (1931) has recorded no change in the frequency of the C — N bond at 1218 cm.$^{-1}$ in the aqueous solutions of pyridine. It is seen from Table I that the reduction in the frequency at 1218 cm.$^{-1}$ in the spectrum of pyridine as recorded by the authors is only of the order of 3 cm.$^{-1}$ But this effect is more pronounced in the case of admixture with phenol whose proton-accepting capacity is much greater than that of either water or methanol.

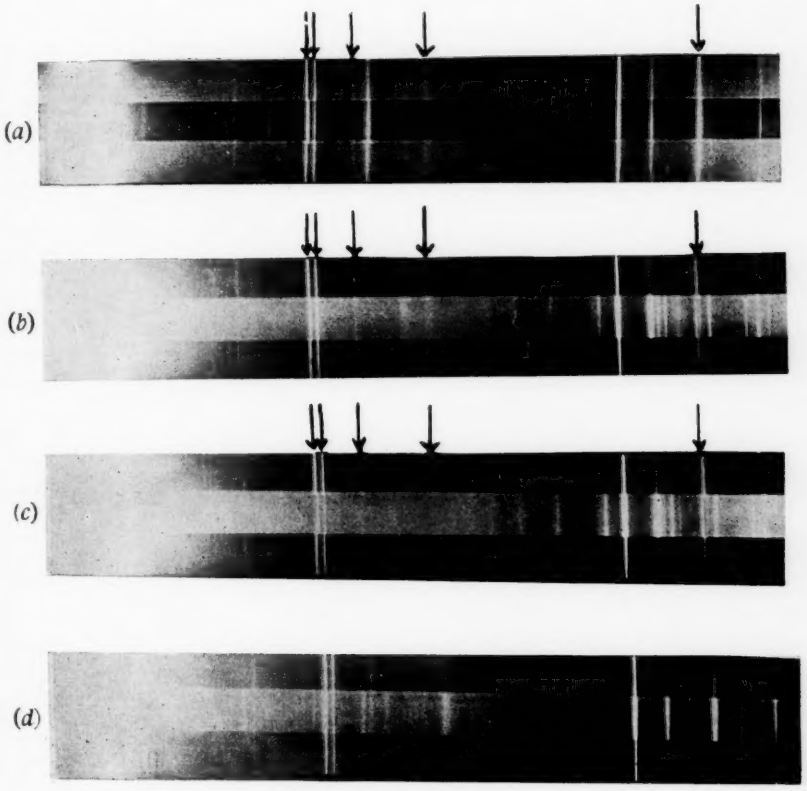
The variation in the intensity of the lines and the background in the spectrum of pyridine-acceptor mixtures shows a behaviour different from that observed in the mixtures of aldehydes, ketones and esters with acceptor solvents. In the case of latter there is a feeble background in the spectrum of mixtures, but in the case of former, even the little background which is present in the specturm of pure pyridine is almost completely eliminated.

In the case of pyridine-dioxane mixtures there is a general reduction in the intensities of both Raman and Rayleigh lines.

The authors express their sincere gratitude to Professor S. Bhagavantam for his illuminating discussions and inspiring guidance during the progress of this work.

VI. SUMMARY

The Raman spectra of pyridine-acceptor mixtures have been investigated and the effect of N- - -H hydrogen bond formation on a number of frequencies of pyridine had been recorded for the first time. The lines at 933, 1218 and 1578 cm.$^{-1}$ have been assigned to the vibrations C — N = C (in plane bending), C — N stretch and C = N in pyridine. The difference between O- - -H hydrogen bond formation and N- - -H hydrogen bond formation has been brought out. It has been suggested that if the hydrogen bond is formed with a member of the ring, the ring gets perturbed resulting in the variation of most of the frequencies attributed to different modes of the vibrations of the ring.



Raman Spectra of Pyridine in mixtures:—
(*a*) Pyridine-Phenol Ratio 1 : 2 by volume
(*b*) Pyridine–Methanol ,, 1 : 2 ,,
(*c*) Pyridine–Water ,, 1 : 2 ,,
(*d*) Pyridine–Benzene ,, 1 : 2 ,,

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